



## 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> <b>Structural origins of barocaloric properties in hybrid plastic crystals</b>	<b>Experiment number:</b> MA 5145
<b>Beamline:</b> BM01	<b>Date of experiment:</b> from: 05 Jul 2022 to: 11 Jul 2022	<b>Date of report:</b> 13 Sept 2022
<b>Shifts:</b> 18	<b>Local contact(s):</b> Charles Mcmonagle	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Charles MCMONAGLE* (Laboratory SNBL-CRG (NOR) c/o ESRF 71 avenue des Martyrs CS 40220 FR - 38043 GRENOBLE Cedex 09) Javier GARCÍA BEN (Laboratory Universidade da Coruna QuiMolMat Group, Dpt. Chemistry CICA, Campus de Elviña ES - 15071 A CORUNA) Jorge SALGADO-BECEIRO (Laboratory Universidade da Coruna QuiMolMat Group, Dpt. Chemistry CICA, Campus de Elviña ES - 15071 A CORUNA) Juan Manuel BERMUDEZ GARCIA (Laboratory Universidade da Coruna QuiMolMat Group, Dpt. Chemistry CICA, Campus de Elviña ES - 15071 A CORUNA) Julian WALKER (Laboratory Norwegian University of Science & Technology NTNU NO – 7491)TRONDHEIM		

### Report:

According to variable-pressure differential scanning calorimetry (VP-DSC), both  $[(\text{CH}_3)_3(\text{CH}_2\text{Cl})\text{N}]\text{FeCl}_4$  and  $[(\text{CH}_3)_3(\text{CH}_2\text{Cl})\text{N}]\text{GaCl}_4$  compounds present a peculiar P vs T phase diagram (see Figure 1), showing a polymorph not stable at ambient pressure, but stable under external pressure. In order to obtain structural information about both compounds, we have carried out variable-pressure synchrotron powder X-ray diffraction (VP-SPXRD) experiments at different temperatures. We have used a custom sample cell developed by ESRF-SNBL postdoc Charlie McMonagle (SNBL BM01 beamline) which provides a very precise pressure control between 1 and 1000 bar under isothermal conditions at different temperatures. For this purpose, the SPXRD patterns were recorded using the 2D Pilatus 2M detector.

Very interestingly, the VP-SPXRD showed clearly multiphase transitions, in agreement with the previous VP-DSC results. In this context, Figure 2 shows the presence of two phase transitions and three different polymorphs for  $[(\text{CH}_3)_3(\text{CH}_2\text{Cl})\text{N}]\text{FeCl}_4$  under compression from 500 bar to 850 bar at 339 K. It is worth to note that one of the polymorphs is different to those reported at ambient pressure. Furthermore, we have carried out a leBail refinement of all obtained patterns at different temperatures and pressures. For the two ambient pressure polymorphs we have concluded that polymorph I (PI) crystallizes in a monoclinic symmetry and space group  $Cm$ , and that polymorph III (PIII) crystallizes in a cubic symmetry and space group  $Pm\bar{3}m$ . Also, we have successfully refined the high pressure polymorph (PII) (see Figure 3) which crystallizes in an orthorhombic symmetry with space group  $Pmm2$ .

Also, we have estimated the evolution of the lattice parameters and volume cell as a function of temperature and applied pressure (see Figure 4).

All the structural information obtained under variable temperature and pressure is currently under analysis, in order to understand the origin of the observed giant barocaloric response of those compounds. In particular, we

are estimating the entropy change arising from both the volume change at the phase transition and the volume change related to the material own compressibility (independent from the phase transition). Both volumetric contributions will allow to separate these from the total entropy change estimated from variable temperature and variable pressure differential scanning calorimetry (VT-DSC and VP-DSC) measurements at isobaric and/or isothermal conditions. We hope to publish soon the obtained results in a high impact journal.

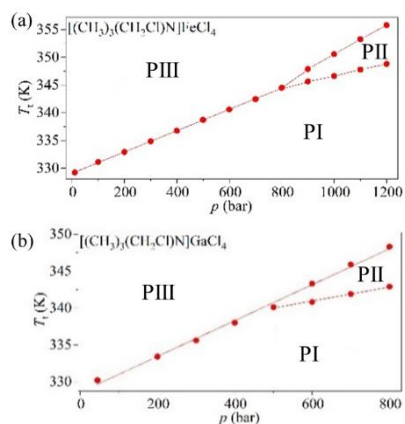


Figure 1. Diagram phase in function of temperature and pressure of (a)  $[(CH_3)_3(CH_2Cl)N]FeCl_4$  and (b)  $[(CH_3)_3(CH_2Cl)N]GaCl_4$ .

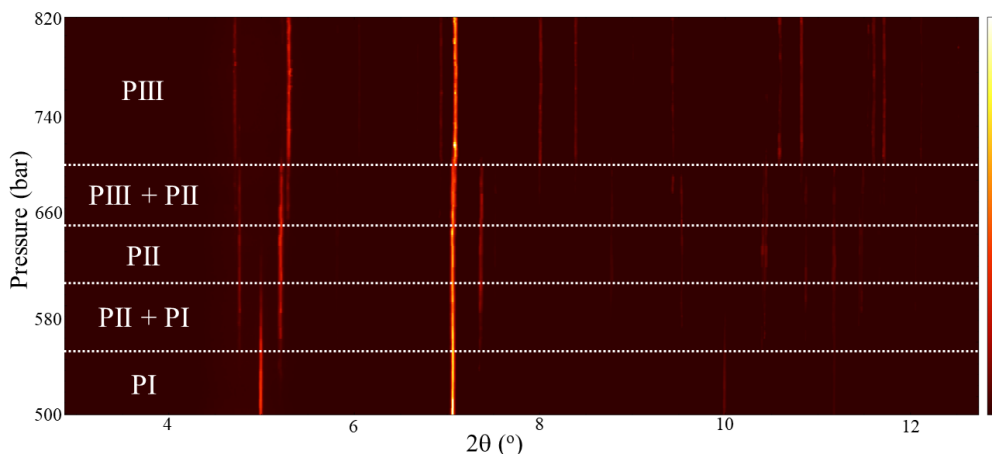


Figure 2. Variable pressure SPXRD patterns of  $[(CH_3)_3(CH_2Cl)N]GaCl_4$  under compression from 500 bar to 850 bar at 339 K.

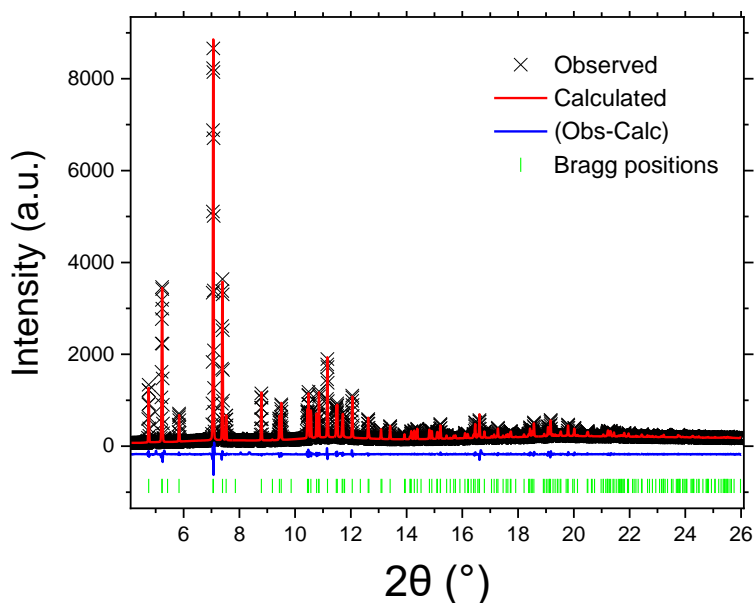


Figure 3. *leBail* refinement of polymorph II for  $[(CH_3)_3(CH_2Cl)N]FeCl_4$  compound obtained at  $p=770$  bar and  $T=339$  K.

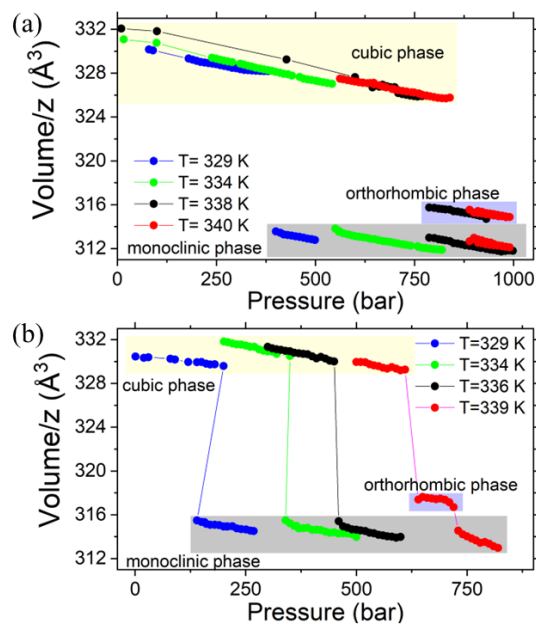


Figure 4. Cell volume in function of pressure and at different temperatures of each polymorphs of (a)  $[(CH_3)_3(CH_2Cl)N]FeCl_4$  and (b)  $[(CH_3)_3(CH_2Cl)N]GaCl_4$ .