

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

- 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.



	Experiment title: Order-disorder Transitions in Tetrafluoroborate Salts – Investigation into Structural Stabilities over Many Temperature Cycling	Experiment number: CH-6552
Beamline: ID22	Date of experiment: from: 08/04/2023 to: 11/04/2023	Date of report: 11-09-23
Shifts: 9	Local contact(s): Andrew Fitch	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr Sumit Konar Instrument Scientist (Solid-state materials) School of Chemistry, Joseph Banks Laboratories, University of Lincoln, Lincoln LN6 7DL, United Kingdom Email skonar@lincoln.ac.uk		

Report:

The results from this beamtime experiment were submitted to Chemistry of Materials, and the manuscript is currently under review. Please keep the report confidential until the results are published.

Summary: In situ synchrotron powder x-ray diffraction (PXRD) study was conducted on sodium and potassium tetrafluoroborate (NaBF₄ and KBF₄) to elucidate structural changes across solid-solid phase transitions over multiple heating-cooling cycles. The phase transition temperatures from diffraction measurements are consistent with the differential scanning calorimetry data (~240 °C for NaBF₄ and ~290 °C for KBF₄). The crystal structure of the high-temperature (HT) NaBF₄ phase has been determined from synchrotron PXRD data. The HT disordered phase of NaBF₄ crystallizes in the hexagonal, space group *P6₃/mmc* (No. 194) with *a* = 4.98955(1)Å, *c* = 7.73498(3)Å, *V* = 166.768(1) Å³, and *Z* = 2 at 250 °C. Thermal expansion coefficients for both phases were determined from high precision lattice parameters at elevated temperatures, as obtained from Rietveld refinement of PXRD data. Interestingly for the HT-phase of NaBF₄, the structure (upon heating) contracts slightly in the *a*-*b* plane but expands in the *c* direction such that overall thermal expansion is positive.

Variable Temperature Powder x-ray diffraction measurements. The samples were contained in 1 mm diameter thin-walled borosilicate glass capillaries that were spun at 919 rpm on the axis of the high resolution powder diffractometer at beamline ID22 at the European Synchrotron Radiation Facility. The X-ray wavelength was calibrated as 0.354331(7) Å (35 keV) via NIST standard 640c Si powder. Diffraction patterns were collected in continuous-scanning mode using the 13-channel Si 111 multianalyser stage at 10 or 20 degrees per minute and recording data every 3 ms or 1.5 ms, respectively. Data were corrected for the effects of axial divergence and the 13 channels were

combined and rebinned into steps of 0.0007 degrees. Heating was via a hot-air blower, and rebinned into steps of 0.0007 degrees.

Rietveld analysis Rietveld analysis of PXRD patterns was performed using the Topas Academic V7. Crystal structures of KBF_4 and NaBF_4 were refined using orthorhombic $Pnma$ and $Cmcm$ space groups, respectively. The scale factor, background parameters, instrumental zero-point, lattice parameters, peak profile parameters (a full Voigt function was used) were initially refined. To fit the highly anisotropic peak shapes Stephens hkl dependent peak shape model was used. In the final Rietveld refinements, all atom positions were reliably refined without restraints Neither set of data would give a stable refinement if the occupation factors and thermal parameters were simultaneously refined. The occupation factors for all the atoms were therefore constrained to achieve charge balance. Isotropic thermal parameters (B_{iso}) for the individual atoms were refined for the ordered structures. However, for the HT disordered phases, B_{iso} for individual atom types yielded high and unreliable values; and therefore, an overall common B_{iso} for all the atoms were set and refined. Thermal expansion coefficients were calculated using the PASCAL program.

Results:

The key findings are summarized in Figure 1 and Figure 2.

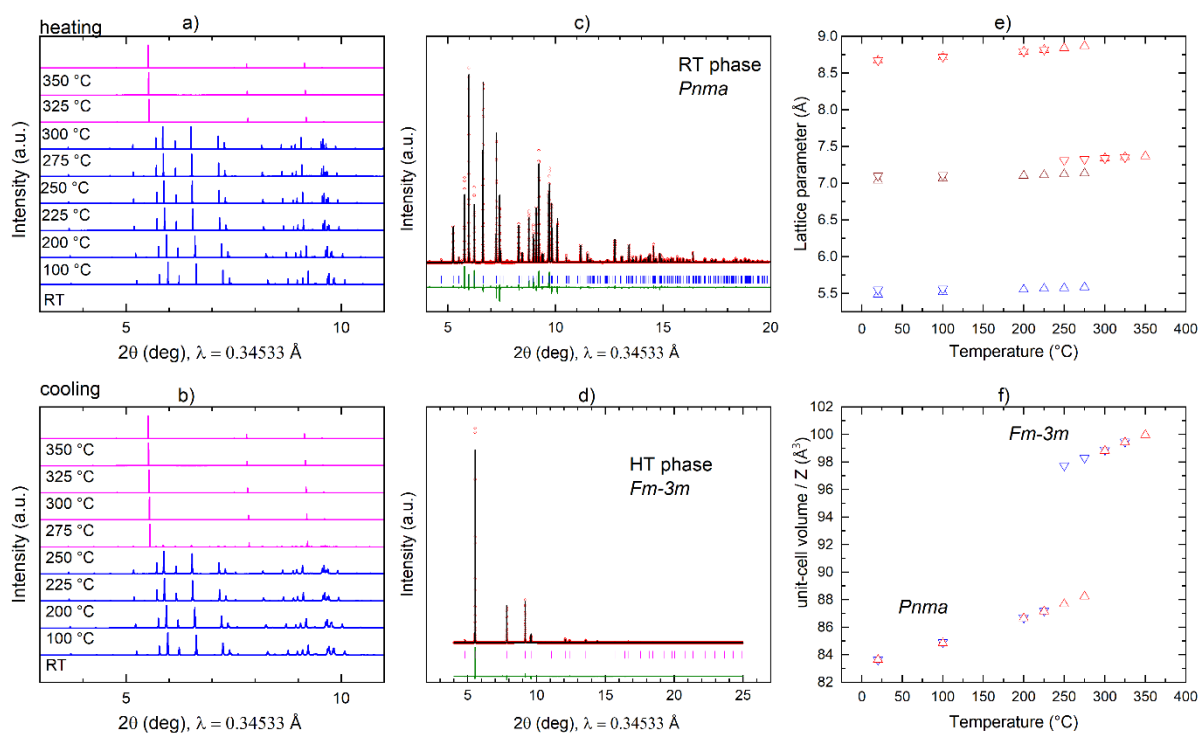


Figure 1 a-b) Compilation of in situ PXRD patterns of KBF_4 at variable temperatures (RT – 350 °C) showing the transition from RT orthorhombic ($Pnma$) to HT cubic ($Fm-3m$) phase during heating and cooling: blue line: $Pnma$ and magenta line: $Fm-3m$; c-d) Rietveld refinement fit of RT and HT-phase of KBF_4 , experimental (observed) data are shown as red dots, the solid black line shows the calculated profile from the refinements, and the bottom green traces show the residual intensities $I(\text{obs}) - I(\text{calc})$. The simulated Bragg reflections for the phases are given as vertical tick marks; e-f) Temperature dependence of the lattice parameters and unit cell volume of LT- and HT- KBF_4 as obtained from synchrotron powder diffraction data; triangles facing up and down represent data from heating and cooling cycles, respectively.

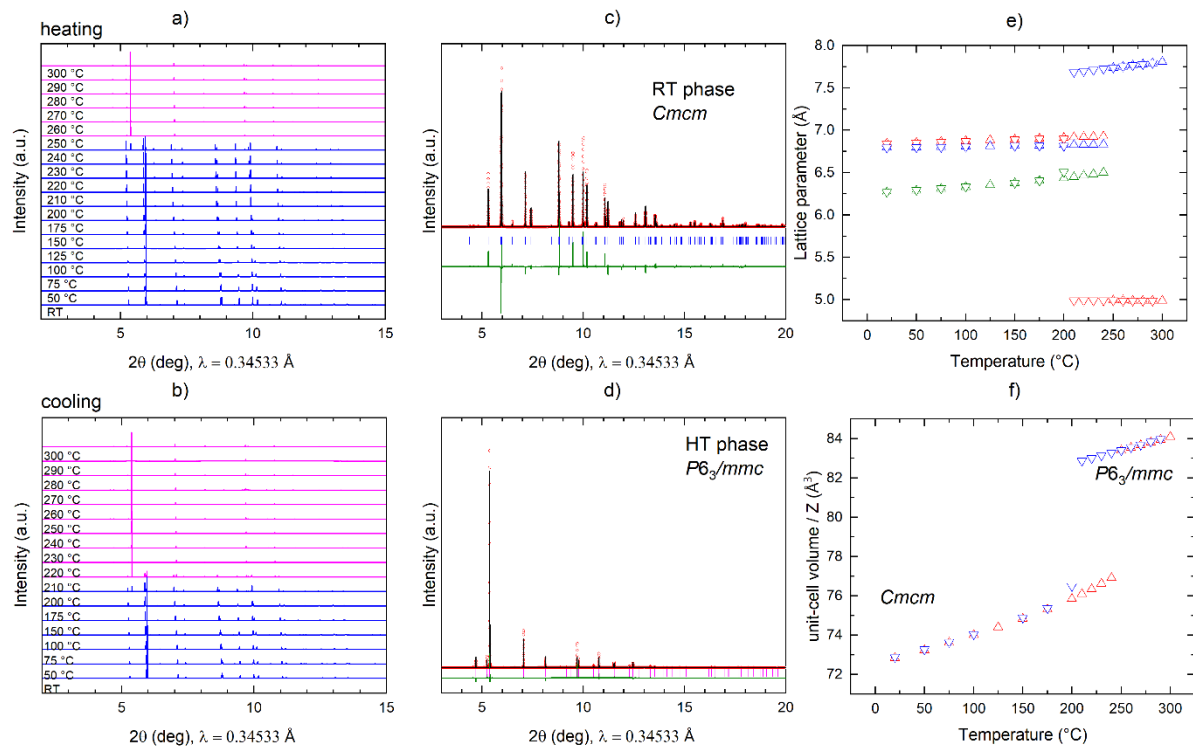


Figure 2 a-b) Compilation of in situ PXRD patterns of NaBF₄ at variable temperatures (RT – 300 °C) showing the transition from RT orthorhombic (Cmcm) to HT hexagonal (P6₃/mmc) phase during heating and cooling: blue line: Cmcm and magenta line: P6₃/mmc; c-d) Rietveld refinement fit of RT and HT-phase of NaBF₄, experimental (observed) data are shown as red dots, the solid black line shows the calculated profile from the refinements, and the bottom green traces show the residual intensities $I(\text{obs}) - I(\text{calc})$. The simulated Bragg reflections for the phases are given as vertical tick marks; e-f) Temperature dependence of the lattice parameters and unit cell volume of LT- and HT-NaBF₄ as obtained from synchrotron powder diffraction data; triangles facing up and down represent data from heating and cooling cycles, respectively