	Experiment title: Pressure-induced structural transition in NaCrF$_3$	**Experiment number**: HC4436
Beamline: ID06-LVP	**Date of experiment**: from: 23.1.2021 to: 26.1.2021	**Date of report**: 03.03.2021
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Report:

The aim of the project was to search for pressure-inded transitions in the highly distored fluoroperovsite NaCrF$_3$, with the exotic Jahn-Teller active Cr(II) cation. This was the first high-pressure experiment on a NaCrF$_3$, or, indeed, for any ACrF$_3$. It was challenging to find the best conditions for the system, yet , we managed to complete five runs of NaCrF$_3$ during the experiment and we gained a lot of insight to the system. In addition, the experiment also opened for new questions and follow-up experiments are desired.

For the first run, we discovered that NaCrF$_3$ is particularly challenging to study at high pressure and temperature. We observed severe grain reconstruction under ver modest load that does not recover at high temperature, nor unloading (so not stress-induced). In addition, use of (fairly standard) B:Epoxy gasket that gave a lot of additional peaks in interesting regions, making it challenging to interpret the data, see Figure 1a. Nevertheless, we observed a transition from the tricilinc structure to a structure of higher symmetry upon heating under a pressure of about 8.4 GPa. The current understanding is that this phase, at that pressure and higher is a GdFeO$_3$ perovskite, yet further investigations is needed to resolve this matter. On further, very moderate, heating, we observed a new phase appearing, identified as a cryolite phase. The cryolite phase is Na$_3$CrF$_6$ phase and indicates decomposition of the perovskite. This mode of occurrence of phase will be discussed in more detail below.
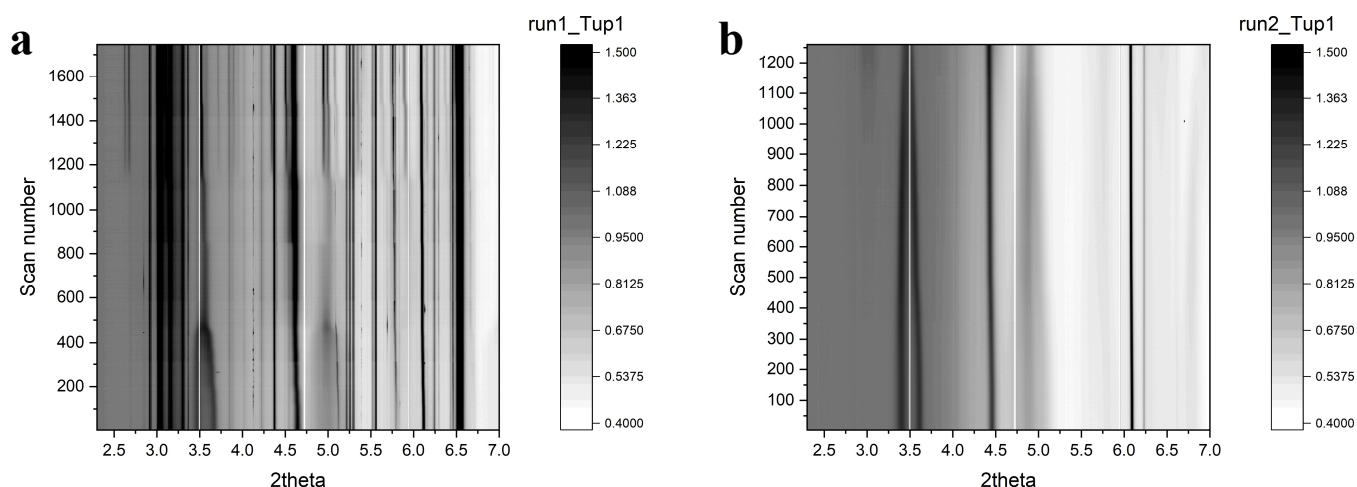

Figure 1: (a) Temperature induced transition at 8.4 GPa. Severe signals from the sample environment is observed. (b) Temperature induced transition at 5 GPa. The peaks The reflections at 3.25 and 3.5° are split by the monoclinic distortion and is observed to merge at higher temperature, indicating a transition to higher symmetry. The two faint peaks at ~3° are those most strongly indicative of a transition to cryolite phase.

For the second run, we aimed for, and achieved, much clearer data, by use of ceramic non-oxide gaskets, Figure 1b. However, this run was performed at about 5 GPa, and we observe a more direct transition from the triclinic perovskite structure to the cryolite phase, which is an intriguing observation, indicating some competition between perovskite and cryolite products. The third run was carried out at 12.5 GPa, to see if we could stabilize and crystalize the $GdFeO_3$ phase at higher pressures, however, we again observed the formation of cryolite, though perhaps via a short-lived intermediate.

For the fourth run, we decided to do a pressure-scan up to 18 GPa to see if we could induce the transition by pressure only, Figure 2a. Indeed, the peak splitting from the triclinic distortion progressively dissapears with applied pressure. Such merging is indicative of a 2nd order, or very weakly 1st order, transformation. This sample was decompressed without heating, to avoid cryolite formation, in order to attempt recovery of the HP phase. It, however, appears to have backtransformed on decompression.
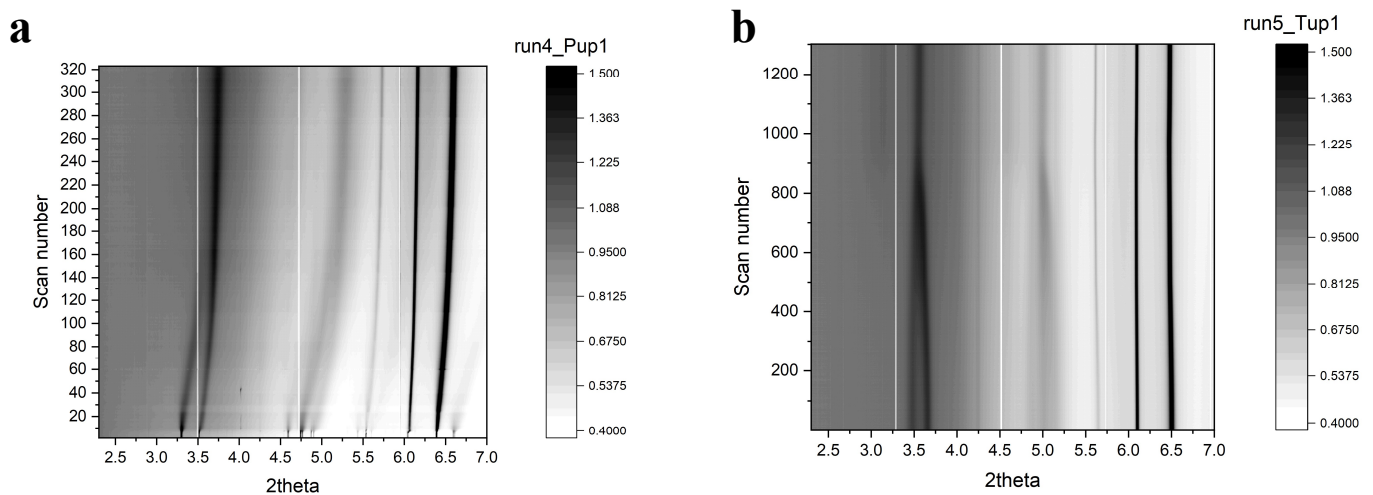

Figure 2: (a) Pressure-induced transition in NaCrF₃ by pressures from 0 to 18 GPa. The reflections at 3.25 and 3.5° are split by the triclinic distortion and are observed to merge when high pressures are applied. (b) Temperature induced transition at 9 GPa. The peaks at 3.45 and 3.2° are merging, indicating a transition from the triclinic Jahn-Teller disordered structure to a higher-symmetry structure, probably of GdFeO₃-type.

For the fifth and final run, we found very good conditions for following the transition to the $GdFeO_3$-type structure without formation of the cryolite phase, Figure 2b. Furthermore, we were able to recover the sample successfully. Why we could recover this and not the sample produced at HP (alone) is unclear. The samples will undergo further investigations to verify the atomic arrangement by TEM and other methods in the home labratory. As we search for pressure induced transitions in $NaCrF_3$, was the transition from the tricilinc $NaCrF_3$- structure to a $GdFeO_3$-phase indicative of the success of the experiment.

For the formation of the cryolite phase, several questions are still remaining. First, we do not observe the formation of Cr metal or/and CrF_x, indicating that the cryolite phase might not have a composition of Na_3CrF_6. Furthermore, preliminary Rietveld refinements support that this might not be the correct composition. We speculate whether a double perovskite with two different Cr sites ($Na_2CrCr'F_6$) is formed, similar as for rare earth nickelates [1] or Fe_2O_3 at high pressures [2]. The two Cr sites may be different with respect to spin or valence state (e.g. $2Cr^{2+} \rightarrow Cr^{2+\delta} + Cr^{2-\delta}$; following [1]). The intensity of the cryolite peaks at ~3° (with respect to the remainder) determines the occupancy of potential lattice-doubling cation site (if Cr then it is weak and a perovskite, if Na it is much stronger and a cryolite). In the case of cryolite *sensu stricto* formation, through decomposition, this peak merging of 110/020 and 1-10 of $NaCrF_3$ does not reach its conclusion and, instead, at phase formation, the peaks are displaced slightly (due to the different lattice volumes) and the low angle peaks at 3° are as intense as the next set of merged peaks at ~3.5° (for Na_3CrF_6 composition). Investigation of two structural options, where the sole topological difference is one sites occupancy for Na or Cr, requires (at least) continuous data collection. Clearly, a $Na_2CrCr'F_6$ perovskite with inequivalent Cr lattice sites (e.g., with mixed spin or valence) is also a cryolite but with retained perovskite stoichiometry. This situation, which is entirely reasonable, is very difficult to observe, given that the diffraction patterns (and structures) of such a cryolite and a $GdFeO_3$ perovskite are near-identical (indeed the only difference is monoclinic splitting with $\beta \sim 90°$). We have requested further beamtime to explore these intreguing behaviours.

References:
1. J. A. Alonso, et al., Phys. Rev. B, **61,** 1756, 2000
2. E. Bykova, et al., High-Pressure Res. **33**, 534, 2013