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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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

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Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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

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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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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:** Systematics in Perovskites to Post-Perovskites Transition	**Experiment number**: HS-3404
Beamline: ID27	**Date of experiment**: from: 06.10.2007 to: 09.10.2007	**Date of report**: 27.02.08
Shifts: 9	**Local contact(s)**: Dr. Mohamed Mezouar	*Received at ESRF:*

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Report:

Recently, we explored structural distortions in perovskite type oxides ABO_3 and have shown how increasing structural distortion expressed in terms of polyhedral volume ratio V_A/V_B results in lowering symmetry from Pm3m to Pnma [1]. Among other things we have established that the most highly distorted perovskite modification Pnma is stable only above $V_A/V_B \sim 3.8$. Further distortion of perovskite structure, for example by applying high pressure, results in transformation to post-perovskite modification as has been recently demonstrated in the case of $NaMgF_3$ [2]. Obviously, the closer the structure to perovskite-post-perovskite phase boundary at ambient conditions, the lower the pressure required to transform that perovskite to $CaIrO_3$-type. Using the structural data accumulated in the Inorganic Crystal Structure Database (ICSD) and ab-initio computer simulations we have identified several perovskites that are highly distorted at ambient conditions that we proposed to study by diffraction under high pressure.

We have investigated pressure-induced structural evolution of $SrPbO_3$ and $NaZnF_3$ using gas-driven diamond anvil cells in the pressure range 0-40 GPa. Pressure was determined by the ruby fluorescence method. One-dimensional spectra were obtained by integration of signal from image plate using FIT2D software.

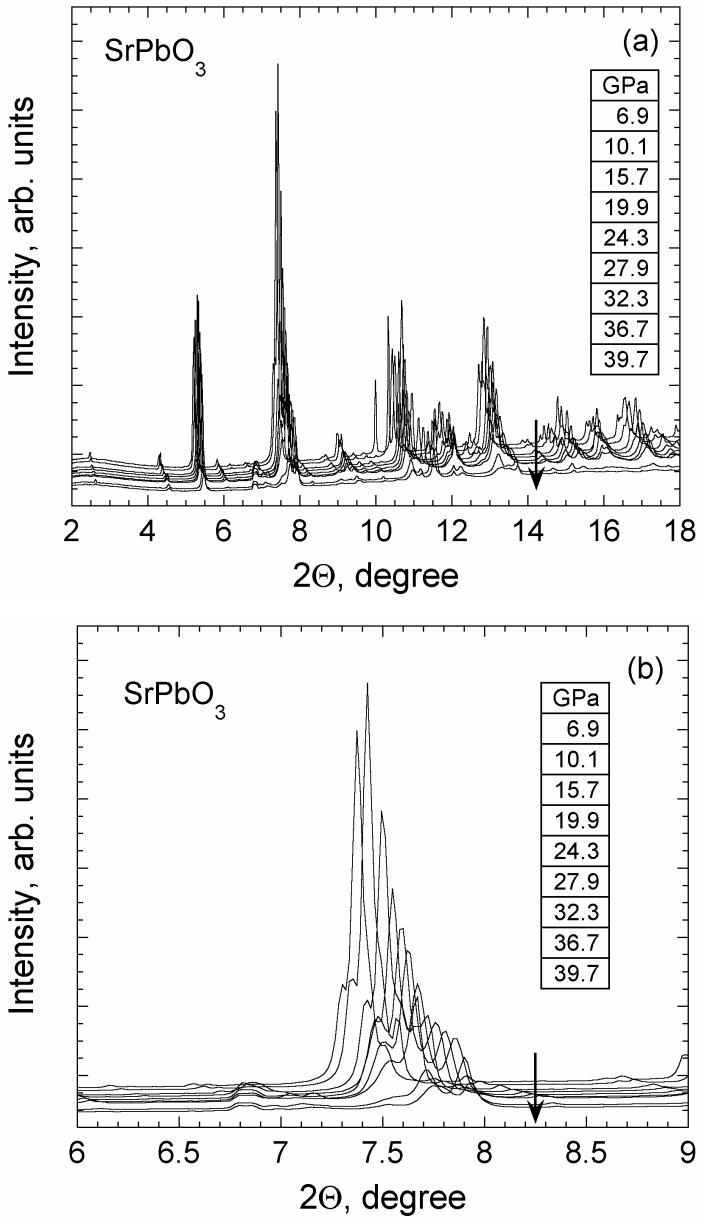

Fig. 1. Pressure-induced variation of X-ray diffraction patterns of $SrPbO_3$: whole patterns (a) and fragments (b). Pressure values (in GPa) are indicated on the plots. Arrows show the directions of the pressure increasing.

Fig. 1 shows selected spectra acquired for $SrPbO_3$ powder at various pressures. Preliminary data analysis revealed next features: (i) peaks are systematically shifted due to decreasing of the unit cell volume; (ii) sample preserves perovskite-type structure in the entire pressure range investigated; and (iii) decreasing of intensity and peak broadening (Fig. 1(b)) is an indication of structural disorder and/or pressure-induced amorphization. Latter effect is reversible; on decompression, shape and intensity of peaks is recovering.

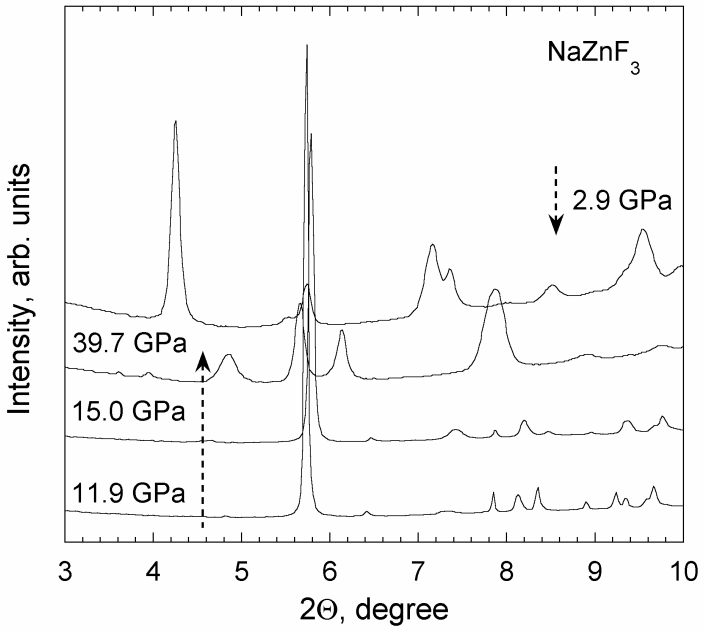

Fig. 2. Selected spectra obtained for NaZnF3 on increasing pressure and on decompression (directions of the pressure variations are indicated with the arrows).

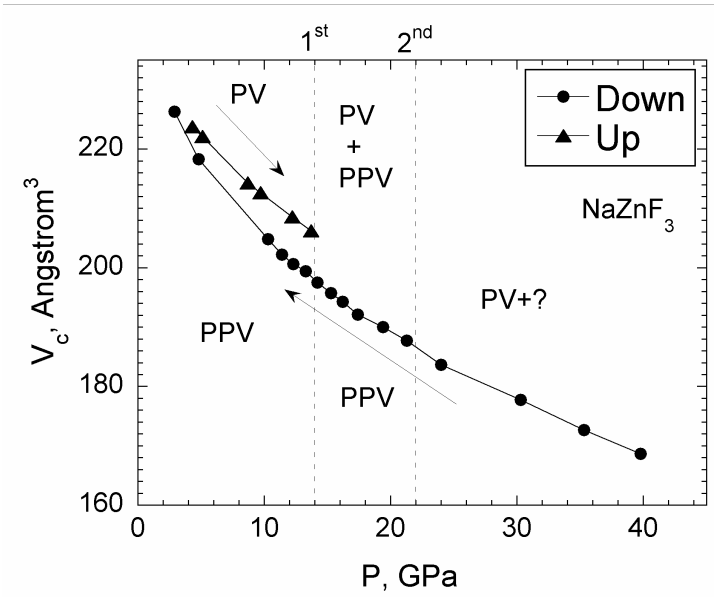

Fig. 3. Pressure dependencies of the cell volumes of perovskite and postperovskite modifications of $NaZnF_3$ (on the compression and decompression).

Fig. 2 shows selected X-ray spectra obtained for $NaZnF_3$ on compression and decompression (directions of pressure variation are indicated by the arrows). For this compound, presumably tho pressure-induced phase transitions were observed. At 10.4 GPa on the compression, perovskite phase begins to transform into the postperovskite. These two modifications of $NaZnF_3$ coexist in the pressure range from 10.4 to 20.2 GPa. Pressure-dependent cell volumes obtained for perovskite and postperovskite phases are represented in Fig. 3. Above 20.3 GPa, post-perovskite coexists with another phase thus far not identified. After the pressure is

released, sample consists in post-perovskite phase only. To our knowledge, this is the first experiment where high-pressure post-perovskite phase was quenched. Fig. 4 shows examplary Rietveld plot corresponding to the data acquired at 2.9 GPa on decompression. Data could be well fitted using post-perovskite structural model (space group Cmcm). Currently, we carry out a series of in situ high-pressure Raman spectroscopy experiments and DFT calculations to complement diffraction data and to clarify the nature of the phase existing above ~22GPa.

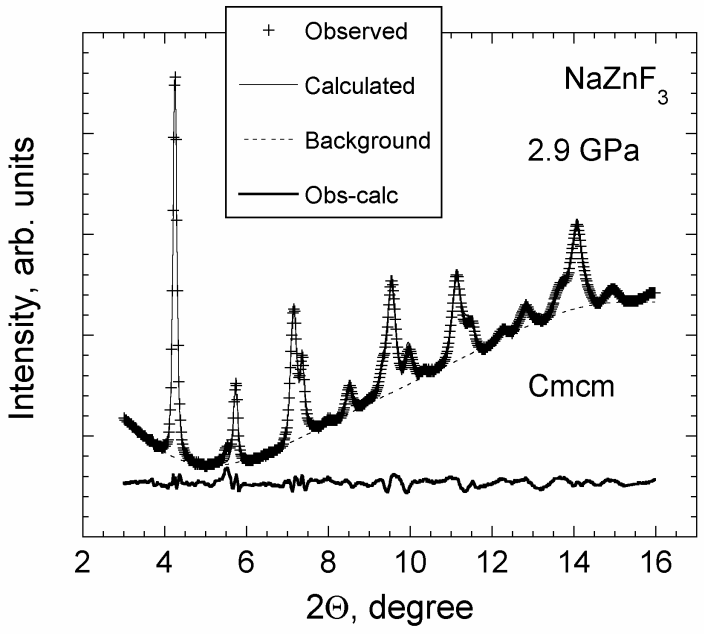

Fig. 4. Example of the Rietveld refinement results of $NaZnF_3$. Spectra was obtained on decompression.

References

1. M. Avdeev, E.N. Caspi, S. Yakovlev, On the polyhedral volume ratios V_A/V_B in perovskites ABX_3, *Acta Cryst. B,* 63, 363 (2007).

2. C.D. Martin, et al., Rietveld structure refinement of perovskite and post-perovskite phases of $NaMgF_3$ (Neighborite) at high pressures, *Amer. Mineralogist.* 91, 1703 (2006).