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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

Reports supporting requests for additional beam time

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

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.

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: Single crystal diffraction experiments on birnessite**	**Experiment number**: CH923
Beamline: ID13	**Date of experiment**: from: 15 nov 2000 to: 17 nov 2000	**Date of report**: 31/08/2001
Shifts: 9	**Local contact(s)**: Dr David Flot	*Received at ESRF:*

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Report:

Birnessite is the most common mineral of the phyllomanganate family. Its structure consists of non-stoechiometric MnO_2 manganese octahedral layers separated by hydrated interlayer cations such as Na, K, Ca... which are easily exchangeable. Structural and chemical properties of birnessite evolve with preparation conditions and/or the nature of interlayer cations. The main structural and chemical properties of birnessites synthesized at low (25°C) and high (up to 1000°C) temperatures are reasonably known from X-ray powder diffraction data. However, specific diffraction features and some details in the structure remain poorly understood, and the present experiment aimed at solving these specific details on high temperature birnessites.

During this experiment, the ability to record good diffraction patterns from 3 high temperature K-birnessite samples (internally named K115, K142, K151) was first assessed. The layer symmetry of these samples differ as a result of their contrasting temperatures of formation (800°C for K151 and K115 and 1000°C for K142).

Because of their very small size (~5µm in their largest dimension) the quality of the selected crystal is difficult to estimate during the mounting stage. As a consequence, several crystals had to be mounted and tested to obtain a crystal suitable for the planned structural determination. Because of the very small crystal size of the crystals, this mandatory step was difficult and time consuming as about 20 crystals had to be mounted and tested for each K-birnessite sample. For each of these samples, diffraction images were collected at different detector distances and with different oscillation ranges to assess the quality of the crystals.

The best results were obtained with the K151 sample. Data sets were measured with the ID13 micro-diffractometer at room temperature with a beam size of 10 micron diameter at 0.780Å. Data were reduced image by image using DENZO. Although data reduction is not straightforward for compounds with a such small unit cell (a=2.848Å c=14.108Å, space group P63/mmc), we have been able to consistently refine the unit cell. We then tried to refine the structure with SHELXL97 (first results: R1 = 0.0896 for 57 Fo > 4sig(Fo) and 0.0900 for all 60 data, wR2 = 0.2292 for all data) but the ratio number of reflections over number of parameters is too low to satisfactorily carry out a complete data analysis.

Diffraction images for the K142 and K115 samples have shown that these two samples are probably twinned or present a modulated structure. In order to understand this phenomena, we recorded diffraction data for several oscillation ranges (5, 10, 20, 45 90 and 180 degrees respectively). We hope that the result obtained with the K151 compound will help us to analyze these data.

In conclusion, we have demonstrated that it is possible to record good quality diffraction data from birnessite single crystals (at least for sample K151) which is an unprecedented results for this manganate family. However, to refine the crystal structure of the selected samples we need to improve the resolution (~0.82 Å at present) either by using a shorter wavelength or by tilting the detector with respect to the beam axis.