EUROPEAN SYNCHROTRON RADIATION FACILITY
INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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. This double-page report will be reduced by ESRF to a one page, A4 format, and will be published in the Annex to the ESRF Annual Report.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the User Office.

When preparing your report, please follow the instructions below:

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- make sure the report does not exceed the space available; tables and figures may be included if you wish.
- for work which is published or which is in press, you may simply include a copy of the abstract together with full reference details. If the abstract is in a language other than English, ensure that you include an English translation.
- bear in mind that the report will be reduced to 71% of its original size. A type-face such as “Times”, 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

Postal address: User Office, ESRF, B.P. 220, F-38043 GRENOBLE Cedex, France.
Telephone: (33) 76 88 25 52; Fax: (33) 76 88 20 20; e-mail: useroff@esrf.fr.

ESRF	**Experiment title:** (Micro)structural determinations of $LixVO(PO_4)_2$ phases that result from electrochemical lithium insertion-deinsertion	**Experiment number**: CH1729
Beamline: BM01B	**Date of experiment**: 04 May 2004 11 May 2004	**Date of report**: 26/02/99
Shifts: 12	**Local contact(s)**: Denis TESTEMALE	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Joel GAUBICHER*, Matthieu DUBARRY*, Philippe MOREAU and Dominique GUYOMARD
Institut des Materiaux Jean Rouxel, 2 Rue de la Houssiniere, BP 32229
44322 Nantes Cedex 03

Report:

Lithium electrochemical intercalation-deintercalation in host structures results most of the time in phase transitions that are either 1st or 2nd order. Displacive structural transitions are associated to small hysteresis whereas hysteresis larger than 0.2V have been reported for reconstructive phase transitions. This experiment mainly concerned $Li_4VO(PO_4)_2$, that exhibits first order structural phase transformations upon Li insertion-removal associated to potential hysteresis values that span from a few mV to more than 1.8V. $Li_4VO(PO_4)_2$ is obtained from $VO(H_2PO_4)_2$ upon a H^+/Li^+ exchange using Li ethanolate solutions.
First structural refinements allowed to determine the structure of $Li_4VO(PO_4)_2$ which is isostructural with that of the protonated form $VO(H_2PO_4)_2$ but with vanadium disordered over two sites (figure 1 a=8.820008(1)Å, c=8.754524(1)Å, P_4/ncc, R_{wp}=14.7%, R_{exp}=12.3%, R_B=6.72%). The structure is also characterized by an increase of the V-O bonds in the c direction as expected from the increase of the c parameter (+10%) upon the ionic exchange. The microstructure was assed from profile analysis using spherical harmonics, specific profiles for (h+k+l)=2n+1 lines (stacking faults) for the size contribution to the FWHM and an axial strain model to take into account the microdeformation contribution. Results clearly showed that starting rod like crystallites of $VO(H_2PO_4)_2$ break apart in the c direction to give parallepipedic like objects. Electrochemical deinsertion of Li^+ from the lithiated form occurs in two steps. Corresponding compounds could be indexed with the same metric. Structural refinements are underway. The overall effect of the delithiation-oxidation is a decrease of the intra-layer distances due to V(IV) oxidation to V(V) and an increase of the inter-layer distances owing to the removal of the polarizing Li^+ ions.
Regarding the insertion process, three new compounds appear but we could not index the corresponding diagrams so far.

This experiment also permit to determine space groups and indexations using Dicvol and Checkcell of two new compounds $LiV_3O_8.H_2O$ (figure 2) (a=15.5719(3)Å, b=7.1676(1) Å and c=12.1413(3) Å, β=91.708(1)°, $P2_1/m$, R_{wp}=6.3%, R_{exp}=5.2%). and a decavandate of lithium (figure 3). (a=17.6243(3)Å, b=10.3259(2) Å and c=9.2277(2) Å, Pnnm, R_{wp}=8.9%, R_{exp}=7.6%). According to the metric the former is presumably of the hewettite type as $Ba_{0.5}V_3O_8.6H_2O$. Ab-initio structural determination is underway.

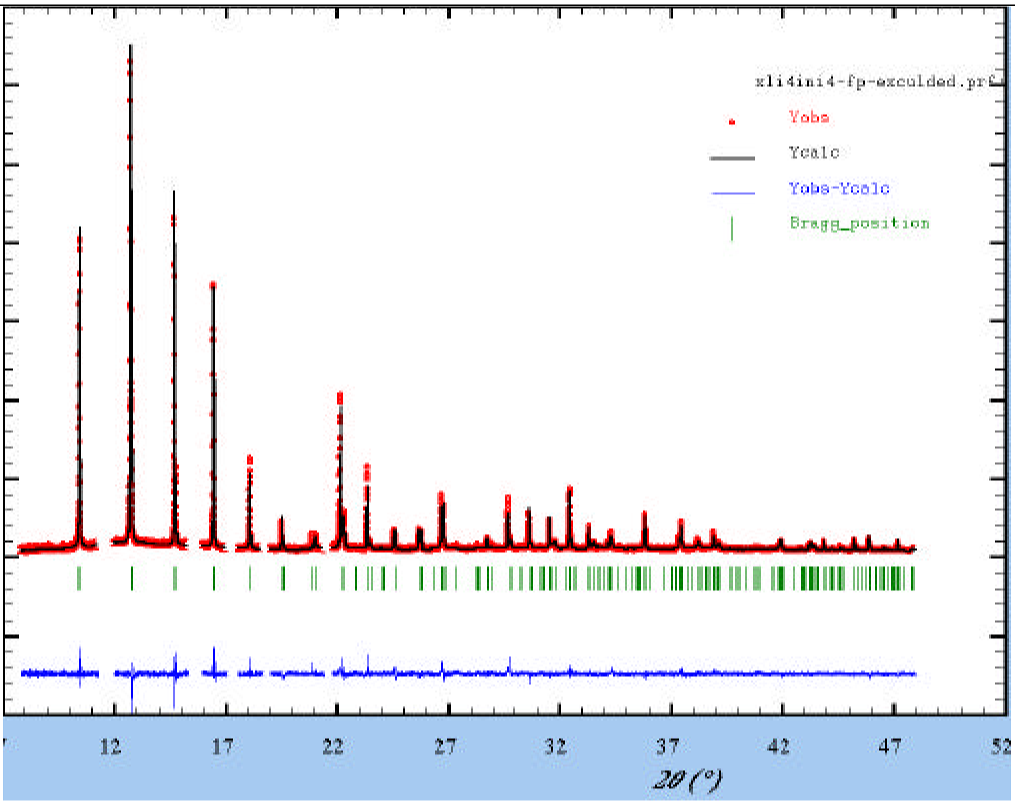

Figure 1: Structural refinement of $Li_4VO(PO_4)_2$ (λ=0.79943 Å).

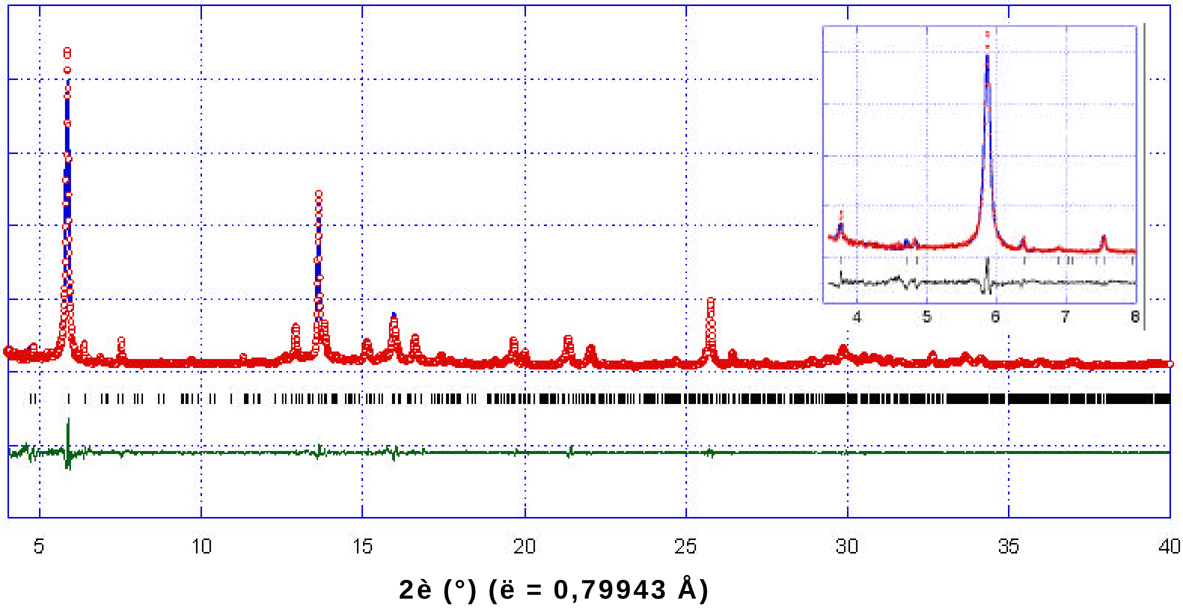

Figure 2: $LiV_3O_8.H_2O$ - Hewettite type.

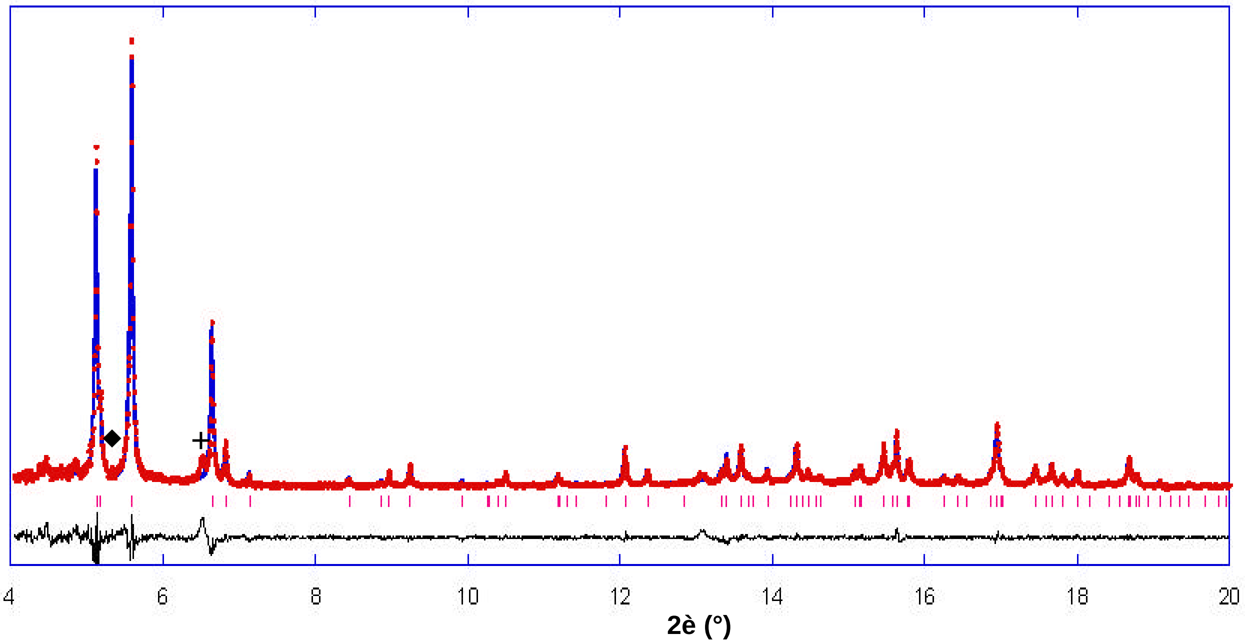

Figure 3: decavandate of lithium (peaks "◆ » and "+" correspond to hewettite like hydrates) (λ=0.79943 Å).