

**Experiment title:***Ab initio* structure determination of new metal phosphonates by powder diffraction**Experiment number:**
CH133**Beamline:**
BM16**Date of Experiment:**

from: 7/8/96 to: 10/8/96

Date of Report:
12/2/97**Shifts:**
8**Local contact(s):**

Eric Dooryhee

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30 JUL. 1997**Names and affiliations of applicants (*indicates experimentalists):**

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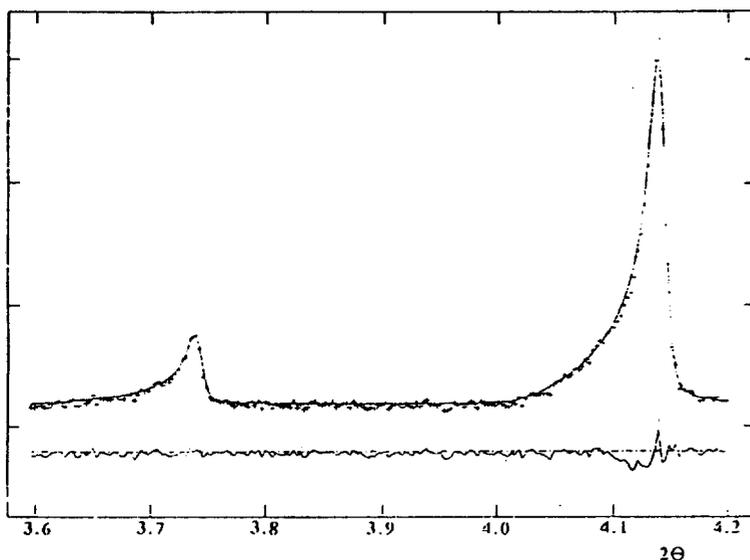
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RESULTS

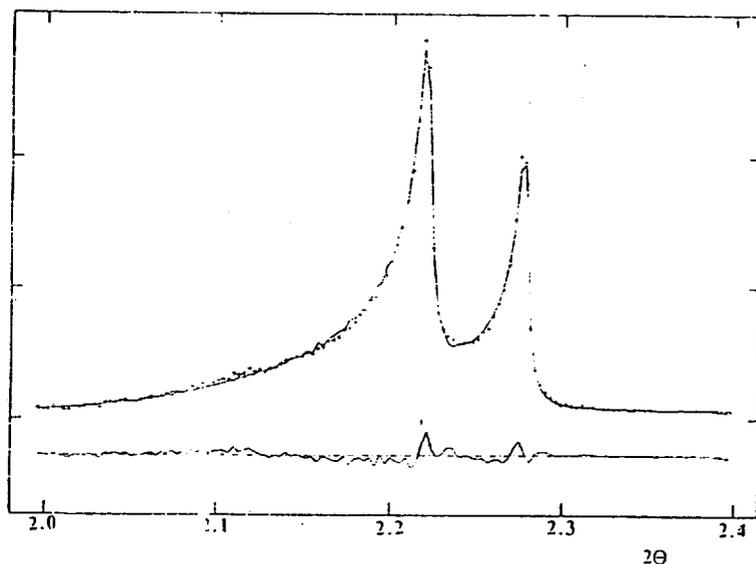
High resolution synchrotron powder patterns were collected on the diffractometer of BM 16 line of ESRF. The samples were loaded in a borosilicate glass capillary ($\phi = 0.5$ mm) and rotated during data collection. A short wavelength, 0.39989(2) Å, selected with a double-crystal Si (311) monochromator, and calibrated with Si NIST, was chosen to reduce the absorption and to get the highest intensity and resolution. Each run took about 10 hours to have good statistics over the angular range 1 to 30 degrees in 2 θ . The data from the nine detectors were normalised and summed up to 0.003 $^{\circ}$ step size with local software to produce the final raw data. The standard geometrical configuration "Debye-Scherrer" was used. The size of the beam on sample was measured with a film: 5.8 mm wide and 0.8 mm height. The distance between the sample and the nine crystal analysers was 442 mm and the distance between the crystal analyzers and the detector slits was 342 mm for the selected short wavelength. The horizontal size of the detector slits were 15 mm. Problems with the monochromator resulted in less intensity on the sample but this was overcome by increasing the counting time. Six patterns were collected in the allocated 8 shifts. One pattern was collected for $\text{Li}_{1.8}(\text{Hf}_{1.2}\text{Fe}_{0.8})(\text{PO}_4)_3$ to carry out a Rietveld refinement and five patterns of metal phosphonates were collected for $\text{Mn}(\text{HPO}_3\text{C}_6\text{H}_5)_2$; $\text{Al}(\text{PO}_3\text{C}_6\text{H}_5)(\text{HPO}_3\text{C}_6\text{H}_5)\text{H}_2\text{O}$; $\text{Pb}_6(\text{PO}_3\text{CH}_2\text{CO}_2)_4$; $\text{Bi}(\text{PO}_3\text{C}_6\text{H}_5)(\text{HPO}_3\text{C}_6\text{H}_5)$; $\text{Pb}_3(\text{P}_3\text{O}_9\text{NC}_3\text{H}_9)_2$; to carry out ab initio structure determinations. Exactly the same experimental set up was used to record the six patterns.

The powder pattern of $\text{Li}_{1.8}(\text{Hf}_{1.2}\text{Fe}_{0.8})(\text{PO}_4)_3$ was refined by the Rietveld method (GSAS - PC program) using as starting model the structure of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$.¹ The very strong peak asymmetry due to

axial divergency was extremely good fitted with the asymmetry correction of Finger, Cox & Jephcoat (1994) (by refining S/L and H/L). *Firstly, overall parameters were refined. Secondly, the structural parameters were optimised and then, the Hf/Fe ratio was varied freely but the Li(1)/Li(2) ratio was refined constrained in such a way that the final value agrees with the Hf/Fe ratio. Hence, electro-neutrality of the formula was ensured. The last refinement was very good: $R_{WP} = 8.11\%$, $R_P = 5.90\%$ and $R_F = 2.5\%$. The variables S/L and H/L are strongly correlated with each other and the zero-shift. The reported standard deviations for S/L and H/L should be taken into account cautiously as they were obtained from refinements with the variables that are very correlated fixed to the final refined value. More details about this refinement and the asymmetry correction is given in a paper submitted for publication.³



This figure shows the Rietveld fit of the first two peaks for $\text{Li}_{1.8}(\text{Hf}_{1.2}\text{Fe}_{0.8})(\text{PO}_4)_3$. The asymmetry parameters were $S/L = 0.0071(4)$ and $H/L = 0.01050(3)$. The FWHM for the first Bragg peak (020) was 0.020° and 0.019° for the second peak (111).



This figure shows the Rietveld fit of the first two peaks for $\text{Mn}(\text{HPO}_3\text{C}_6\text{H}_5)_2$. The asymmetry parameters were $S/L = 0.00846(1)$ and $H/L = 0.00841(1)$. The pattern presented anisotropic peak broadening as evidenced by a FWHM of 0.018° for (110), and 0.013° for (200) which it has been taken into account.

The *ab initio* structure determinations for the metal phosphonates are in progress and the results will be published elsewhere.

- (1) BYKOV, A.B. et al. (1990). *Solid State Ionics* 38, 31-52.
- (2) FINGER, L.W., COX, D.E. & JEPHCOAT, A.P. (1994). *J. Appl. Cryst.* 27, 892-900.
- (3) ARANDA, M.A.G., LOSILLA, E.R., CABEZA, A. & BRUQUE, S. (1997). *J. Appl. Cryst.* submitted