

# A neutron powder diffraction study of electrochemically lithiated R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> for $x = 1.8$

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The electrochemically lithiated form of R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, synthesised by ion exchange of fine powders of Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> in a concentrated aqueous solution of LiNO<sub>3</sub> at a slightly elevated temperature (40 °C), has been investigated by a combination of *ex situ* X-ray and neutron diffraction to probe particularly the lithium-ion distribution in the structure. Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> samples were extracted from discharged electrochemical cells with a Li-metal anode; their structure was refined by the Rietveld method. Approximately 1.8 Li per formula unit can be inserted reversibly into the structure, corresponding to the reduction of almost all Fe<sup>3+</sup> to Fe<sup>2+</sup>. *Ex situ* X-ray powder diffraction shows the Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> framework to remain intact during lithiation. The Li(18f) site in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (space group:  $R\bar{3}$ ) is totally vacated in R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>,  $0 \leq x \leq 1.8$ , with the lithium ions moving into two new general (18f) positions, Li(1) and Li(2), with 74(4)% and 86(4)% occupation, respectively. This corresponds to the Li<sup>+</sup> ions moving cooperatively from pairs of layers (alternate separations: 2.2 and 5.4 Å) for  $x = 0$  to equally spaced layers (separation: 3.8 Å) for  $x = 1.8$ .

## Introduction

Different iron-containing compounds have been studied as potential cathode materials for rechargeable lithium-ion batteries.<sup>1</sup> Such compounds are attractive because iron is abundant, inexpensive and less toxic, particularly compared to Co, Ni and V. Ideally, the layered LiFeO<sub>2</sub> would be preferred as it would operate on the Fe<sup>4+</sup>/Fe<sup>3+</sup> redox couple. However, its electrochemical performance is not impressive due to the metastable nature of its layered structure.<sup>2</sup> This has provoked the investigation of framework structures involving larger polyanions.<sup>3</sup> A series of lithium-containing compounds incorporating polyanions, (XO<sub>4</sub>)<sup>3-</sup> for X = S, P and As, has recently been investigated; most notable of these are the rhombohedral modifications of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub><sup>1,4</sup> and Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>,<sup>5,6</sup> and orthorhombic LiFePO<sub>4</sub>.<sup>5,7,8-11</sup> The SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> polyanions would seem to stabilise the structure and hinder the dissolution of Fe ions. The ordered olivine-type structure, LiFePO<sub>4</sub>, with its relatively high theoretical capacity of 170 mAh g<sup>-1</sup> and flat voltage curve (at *ca.* 3.5 V vs. Li/Li<sup>+</sup>) has emerged as a most promising candidate cathode material for rechargeable lithium-ion (polymer) batteries.

The insertion of lithium into R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> proceeds reversibly for approximately  $0 \leq x \leq 1.8$  at an average voltage of 2.8 V; this would correspond to a discharge capacity of 128 mAh g<sup>-1</sup> if all Fe<sup>3+</sup> were reduced to Fe<sup>2+</sup> ( $x = 2$ ). This material also has a reasonably good response at even high current densities. R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> has been prepared by three successive ion exchanges from the monoclinic sodium compound Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> in a LiNO<sub>3</sub> melt at 300 °C for 1 h, with each exchange followed by extensive rinsing in water.<sup>12</sup> The structure of R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> has recently been solved from neutron powder diffraction data;<sup>13</sup> it has space group  $R\bar{3}$ , with hexagonal cell parameters:  $a = 8.3162(4)$  Å and  $c = 22.459(1)$  Å. R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is isotypic with Li<sub>3</sub>In<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>,<sup>14</sup> its structure comprises PO<sub>4</sub> tetrahedra and FeO<sub>6</sub> octahedra connected through their vertices to form ‘lantern units’ of [Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] stacked in the *c*-direction.

The different space groups of  $\gamma$ -Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> ( $R\bar{3}c$ ) and R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> ( $R\bar{3}$ ) are a result of different cation distributions within the [Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] framework.<sup>15</sup> In R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>,

the Li atoms occupy one 18f site, and the Fe atoms two independent 6c sites. It has been shown that *ca.* 2 extra lithium ions can be inserted to form R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The Li insertion occurs in one continuous step,  $0 \leq x \leq 1.8$ , along a plateau at *ca.* 2.8 V. The Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> framework remains intact under lithium insertion to R-Li<sub>4.8</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and subsequent extraction back to R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.<sup>16</sup>

We report here a structural study of electrochemically inserted R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> for  $x = 1.8$ , using *ex situ* X-ray and neutron powder diffraction.

## Experimental

### Synthesis

The parent compound Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was prepared by direct decomposition and solid-state reaction of Fe<sub>2</sub>O<sub>3</sub> ( $\geq 99\%$ , Merck), NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O ( $\geq 99\%$ , Merck)<sup>13,15</sup> in the molar ratio 1:3.6:2.2. The mixture was heated at 960 °C for 6 h and then cooled to room temperature for ~15 h. The resulting product was dissolved in water and washed thoroughly to dissolve excess sodium phosphates. R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was then obtained by ion-exchanging the fine Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> powder in a concentrated aqueous solution of LiNO<sub>3</sub> at slightly elevated temperature (35–40 °C) for at least 14 h. This ion-exchange procedure was performed three times, washing with water in between. The hexagonal cell parameters (obtained from X-ray powder diffraction) were:  $a = 8.3099(2)$  Å and  $c = 22.5302(9)$  Å, and the effective chemical formula was Li<sub>2.93</sub>Na<sub>0.04</sub>Fe<sub>2.00</sub>(PO<sub>4</sub>)<sub>3</sub> (obtained from ICP analysis).<sup>17</sup>

### Cell preparation

Cathodes were made by spreading a mix of R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, Shawinigan Black (SB) carbon powder and EPDM rubber binder (ratios 80:15:5) in cyclohexane (ball-milled for 1 h) onto an Al-foil current-collector, pre-coated with a suspension of fine carbon particles in an organic binder. The R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> loading on the current collector was 6–7 mg cm<sup>-2</sup>. The electrodes were dried overnight at 80 °C and cut into 2.0 cm diameter discs; the electrodes were again vacuum dried at

120 °C. The cell assembly was carried out in an Ar-filled glove box (<3 ppm H<sub>2</sub>O and O<sub>2</sub>), in which the cathode was laminated against a glass-wool separator soaked in electrolyte and pressed onto a lithium-foil counter electrode, to give half-cells of type <Li |liq. el. |R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>>. The laminates were packed in polymer-coated aluminium bags, evacuated and sealed to give so-called “coffee-bag” type cells. The liquid electrolyte used was 1 M LiBF<sub>4</sub> (Tomiyaama) in EC/DMC 2 : 1 (Selectipur<sup>®</sup>, Merck, Darmstadt, Germany).

### In situ X-ray diffraction

X-Ray diffractograms were obtained for half-cells under charge and discharge using an automatic STOE & Cie GmbH STADI powder diffractometer equipped with a small, straight-wire position sensitive detector (~7° in 2θ). Exposures (18 h) were made in transmission mode with Ge-monochromatized CuK<sub>α1</sub>-radiation using a specially designed battery holder for *in situ* measurements.<sup>18</sup> The 2θ-range monitored was 13.0–45.0°. The cell charge/discharge was controlled by a MacPile<sup>™</sup> potentiostat and the current applied was 2.3 mA g<sup>-1</sup>. After discharging, the cell was allowed to equilibrate for 10 h at the open-circuit voltage prior to the XRD measurements.

### Ex situ neutron powder diffraction

The electrochemical insertion of additional lithium into the Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> framework structure was performed with <Li |liq. el. |R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>> half-cells assembled in an argon-filled glove box. Charging/discharging was controlled by a MacPile<sup>™</sup> potentiostat. The cell was discharged in potentiostatic mode (5 mV steps); the potential was increased when the current fell below ~0.2 mA g<sup>-1</sup>. When the potential reached 2 V, the cell was disconnected and left to relax. The cell was dismantled in an argon-filled glove box (<2 ppm H<sub>2</sub>O/O<sub>2</sub>); the cathode materials were then scraped carefully from the aluminium current-collectors and sealed into vanadium tubes. Neutron powder diffraction data were collected at the steady-state medium-flux research reactor R2 in Studsvik, Sweden. A monochromatic system was used involving two copper crystals (220 reflection) in parallel alignment (λ = 1.47 Å). Diffractograms were collected at 60 K in the 2θ range 4.00–139.92° in steps of 0.08°. Data were also collected on the initial R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> powder at 295 K, all experimental conditions were otherwise identical.

### Structure refinement of neutron diffraction data

Rietveld refinements of the R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> data were performed using the program FULLPROF<sup>19,20</sup> in the 2θ-range 8–120°. Neutron scattering lengths used were Li: -1.90, Fe: 9.45, P: 5.13, O: 5.803 fm. Individual diffraction peak profiles were described by a pseudo-Voigt function; a Lorentzian contribution to the Gaussian peak-shape was also refined. A peak asymmetry correction was made for 2θ angles below 45°. Background intensities were described in different ways: for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> data, a polynomial expression  $y_i = \sum B_m [(2\theta_i/90) - 1]^m$  was used, where  $0 \leq m \leq 5$ ; the  $B_m$  coefficients for  $m = 0-4$  were refined together with a scale factor and a 2θ zero-point parameter. The background for the “3 + x” data was described by a linear interpolation between 69 background points. This “manual” technique was necessary because of the irregularity of the background due to the incoherent contribution from the hydrogen atoms in the electrolyte and binder.

The atomic coordinates for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> in space group  $R\bar{3}$ <sup>13</sup> were used as the starting model for the Rietveld refinement. The [Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] “lantern unit” atoms were first refined. Reasonable lithium positions were derived from difference Fourier maps, assessed on the basis of bond-length criteria; these were included in subsequent Rietveld refinements in

which the initial occupancy factors for the two independent Li positions found were initially constrained to correspond to the total charge passed during electrochemical intercalation of R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, together with lithium atoms from the original M(3) site;<sup>13</sup> in total: 4.6 Li. Since occupancy and displacement parameters are highly correlated, isotropic displacement parameters for Li atoms were initially fixed in the refinements of the “3 + x” phase to the values obtained from the refinement of R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The thermal displacement parameters for the lithium atoms were first refined to satisfactory agreement factors and reasonable thermal parameter values. The isotropic thermal parameters were then kept constant, to allow the refinement of the occupancy factors, so that the amount of lithium per formula unit was 4.6, as obtained from electrochemistry.<sup>17</sup> During the analysis of the difference Fourier maps, it was confirmed that no lithium remained in the M(3) site of R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The isotropic thermal displacement parameters for P, O(1), O(2) and O(3) took values large enough to indicate some kind of disorder affecting the (PO<sub>4</sub>)<sup>3-</sup> group. A disorder model was tested with each oxygen atom (O) treated as two separate atoms; no significant improvement was found, and the individual <P–O> distances were either too short or too long. Anisotropic thermal displacement parameters were then introduced; keeping the atomic position of P constant, six anisotropic thermal displacement parameters were refined for P, O(1), O(2) and O(3). The refinement converged with reasonable <P–O> distances. In a final refinement, the atomic position for P was allowed to refine, but the refinement diverged.

## Results and discussion

### Electrochemistry

Fig. 1 shows the first discharge curve for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (potentiostatic mode). The curve exhibits two features: one flat plateau at around 2.8 V, followed by a second more sloping plateau around 2.60–2.65 V. It was possible to insert *ca.* 1.6 Li<sup>+</sup> per formula unit (based on the charge passed through the cell). Two peaks were observed at around 2.80 V and 2.65 V in the corresponding dx/dV plot. A smaller peak could also be distinguished at 2.70 V.<sup>17</sup> These results compare well with recent results of Masquelier *et al.*,<sup>16</sup> except that the feature around 2.70 V is more pronounced in their study.

### X-Ray powder diffraction

The X-ray powder diffractograms obtained from R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, for x = 0 and 1.6, are shown in Fig. 2. It could clearly be verified that the starting material was indeed phase pure R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>; the lattice parameter values (a = 8.309(9); c = 22.530(2) Å) agree well with values obtained

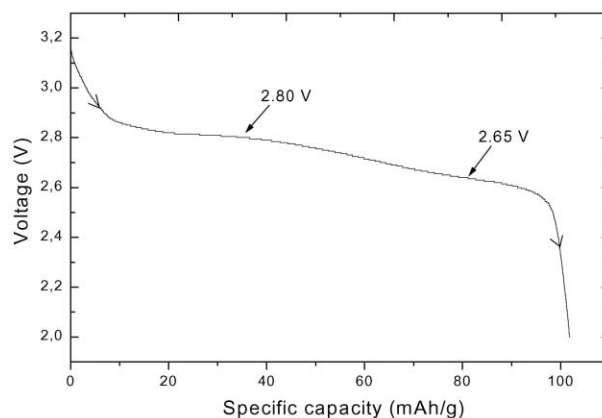
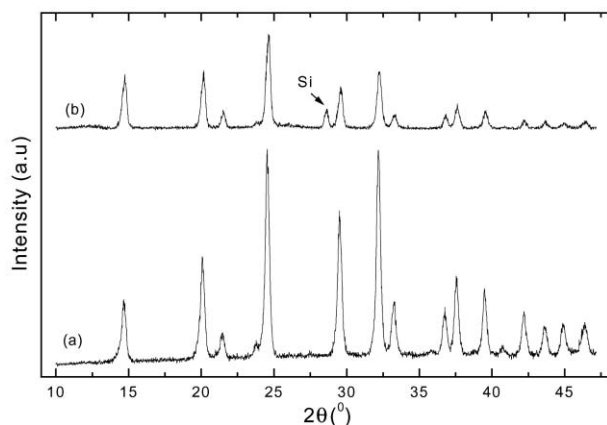


Fig. 1 Discharge curve for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.



**Fig. 2** *Ex situ* X-ray diffractograms for half-cells of R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (a) before discharge ( $x = 0$ ), and (b) after discharge ( $x = 1.6$  Li). CuK<sub>α1</sub>-radiation ( $\lambda = 1.540598$  Å).

from neutron powder data.<sup>13</sup> It is clear from the *ex situ* X-ray powder diffraction data for R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> that the [Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] framework remains intact during lithiation; the peak positions shift only slightly towards lower angles, accompanied by some peak broadening and a decrease in peak intensities, which can be related to increased disorder in the

**Table 1** Overall parameters and Rietveld refinement agreement factors from neutron powder diffraction ( $\lambda = 1.470$  Å) for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>

	R-Li <sub>3</sub> Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> (295 K)	R-Li <sub>3+x</sub> Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> (60 K)
Space group	$R\bar{3}$	$R\bar{3}$
$a/\text{Å}$	8.3009(5)	8.288(2)
$c/\text{Å}$	22.502(2)	22.542(6)
$V/\text{Å}^3$	1342.8 (1)	1341.0(6)
No. of ref. params.	44	55
$R_p$ (%)	3.54	1.89
$R_{wp}$ (%)	4.61	2.36
$R_{exp}$ (%)	2.90	1.59
$\chi^2$	2.52	2.19
$R_{Bragg}$ (%)	4.02	9.30

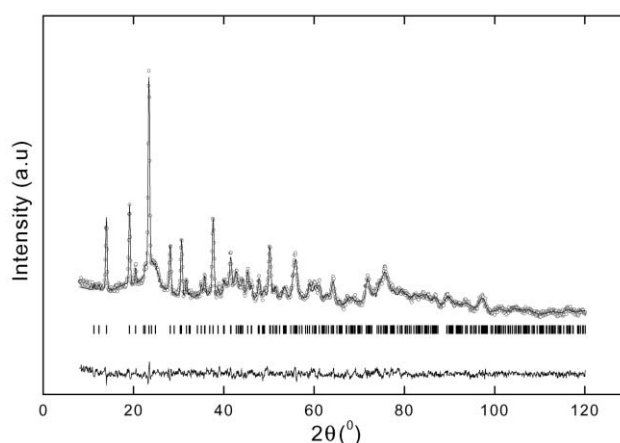
**Table 2** Atomic coordinates and isotropic thermal displacement parameters ( $B$ ) for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (upper row) and R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (lower row) with selected anisotropic thermal displacement parameter ( $10^4 \beta_{ij}$ ) for the “3 +  $x$ ” case

Atom	Site	$x$	$y$	$z$	$B/\text{Å}^2$
Fe(1)	6c	0	0	0.1468(3)	0.174(4)
		0	0	0.147(8)	2.1(4)
Fe(2)	6c	0	0	0.6503(3)	0.28(7)
		0	0	0.647(9)	2.21(4)
P	18f	0.2909(6)	0.0009(7)	0.2500(3)	0.36(8)
		0.298(3)	0.008(4)	0.254(1)	<sup>a</sup>
O(1)	18f	0.1909(7)	-0.0098(6)	0.1928(2)	1.03(9)
		0.208(3)	0.011(3)	0.197(8)	<sup>a</sup>
O(2)	18f	0.7670(7)	0.9108(7)	0.7007(2)	1.04(9)
		0.767(3)	0.901(2)	0.699(7)	<sup>a</sup>
O(3)	18f	0.2414(6)	-0.1977(6)	0.2685(2)	0.69(9)
		0.250(2)	-0.179(3)	0.263(7)	<sup>a</sup>
O(4)	18f	0.4991(6)	0.8799(6)	0.7556(2)	0.55(9)
		0.491(2)	0.881(2)	0.753(6)	1.348(2)
Li	18f	0.347(3)	0.034(3)	0.384(1)	<sup>a</sup>
Li(1) <sup>b</sup>	18f	0.243(9)	0.458(9)	0.096(3)	1.03(5)
Li(2) <sup>b</sup>	18f	0.377(6)	0.136(5)	0.079(2)	1.03(5)

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Li	241(56)	221(56)	10(4)	212(49)	25(14)	23(13)
P	132(58)	245(76)	35(8)	114(49)	-42(22)	-9(17)
O(1)	198(80)	703(131)	12(5)	-288(100)	61(16)	-53(23)
O(2)	422(102)	305(84)	29(8)	-95(69)	98(23)	-97(22)
O(3)	368(86)	377(93)	33(7)	340(72)	41(22)	0.6(21)

<sup>a</sup>Refined anisotropically (see values below). <sup>b</sup>Li(1) and Li(2) occupancies in R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> are 74(4)% and 86(4)%, respectively.



**Fig. 3** Observed, calculated and difference neutron powder diffraction profiles for R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> ( $\lambda = 1.47$  Å).

structure. The *ex situ* X-ray powder diffraction data for R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> show no extra peaks, suggesting no superlattice formation.

### Neutron powder diffraction

Rietveld refinement was performed on the neutron powder diffraction data for R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> for both  $x = 0$  and  $x = 1.8$ , starting with the structure given by Masquelier *et al.*<sup>13</sup> This was done in the space group  $R\bar{3}$ ; the parameters obtained are given in Table 1. The parameters so obtained were then used as starting values for the refinement of the “3 +  $x$ ” data. The observed, calculated and difference neutron powder diffraction profiles for the “3 +  $x$ ” phase are shown in Fig. 3. The final agreement factors and fractional coordinates are listed in Tables 1 and 2. Selected interatomic distances are compared with the corresponding R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> structure obtained from neutron powder data (Table 3).

### The R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> structure

The crystal structure of electrochemically lithiated R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> for  $x = 1.8$  has been determined at 60 K by neutron

**Table 3** Selected bond lengths (in Å) for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>

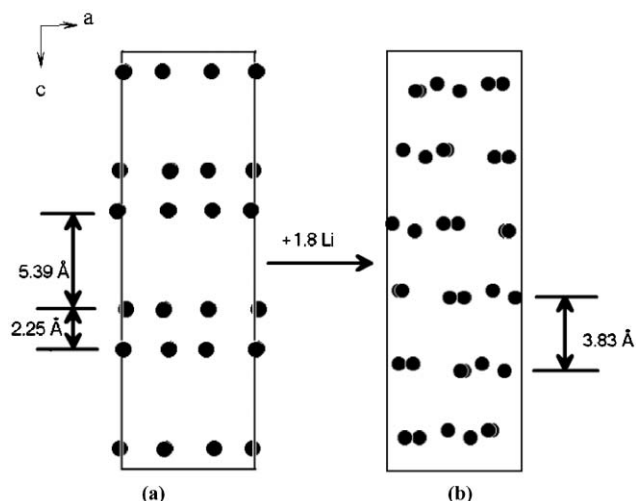
	R-Li <sub>3</sub> Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> (295 K)	R-Li <sub>4.8</sub> Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> (60 K)
Li–O(2)	1.94(3)	Li(1)–O3 (× 2) 2.096(3)
Li–O(2)	2.27(2)	Li(1)–O4 (× 2) 1.743(4)
Li–O(3)	1.89(2)	Li(2)–O1 (× 2) 1.888(2)
Li–O(4)	2.01(2)	Li(2)–O4 (× 2) 2.308(5)
<Li–O>	2.03	<Li(1)–O> 1.919 <Li(2)–O> 2.098
Fe(1)–O(1) × 3	1.929(7)	2.01(2)
Fe(1)–O(4) × 3	2.071(6)	2.10(2)
<Fe(1)–O>	2.00	2.05
Fe(2)–O(2) × 3	2.034(7)	2.05(3)
Fe(2)–O(3) × 3	1.974(6)	2.07(2)
<Fe(2)–O>	2.004	2.06
P–O(1)	1.509(9)	1.503(4)
P–O(2)	1.536(8)	1.514(3)
P–O(3)	1.544(7)	1.476(3)
P–O(4)	1.519(8)	1.498(4)
<P–O>	1.527	1.498

powder diffraction. Masquelier *et al.*<sup>13</sup> have shown that the loss in symmetry on going from space group *R*3̄*c* for Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> to *R*3̄ for R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> corresponds to a splitting of the unique iron site of the sodium analogue into two independent iron sites, Fe(1) and Fe(2), each still lying on the 3-fold axis. One crystallographic site is retained for P and each of the two oxygen sites of the sodium analogue is split into two independent sites, O(i) and O(i'). Our suspicion is maintained of the presence of some more subtle disorder affecting the PO<sub>4</sub> groups, but this cannot be verified with the poor quality powder data available.

The M(1) site of Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> also splits into two M(1a) and M(1b) sites, both unoccupied in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The lithium atoms occupies one crystallographic 18f site in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> which is slightly shifted ( $\sim \pm 0.8$  Å) along the *z*-axis from M(2). In R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, a global redistribution of the lithium sites occurs within the [Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>]<sub>∞</sub> framework. It is known that Na<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> undergoes such order/disorder rearrangements on its sodium sites during the phase transitions:  $\alpha \leftrightarrow \beta$  at 368 K and  $\beta \leftrightarrow \gamma$  at 418 K.<sup>12,15</sup> Both the M(1) and M(2) sites of the NASICON structure remain empty on going from R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> to R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. This behaviour has been seen previously in the M(1) site in the LiIn<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> → Li<sub>3</sub>In<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> transition, although there are no reports of a vacancy at the M(2) site.<sup>21</sup>

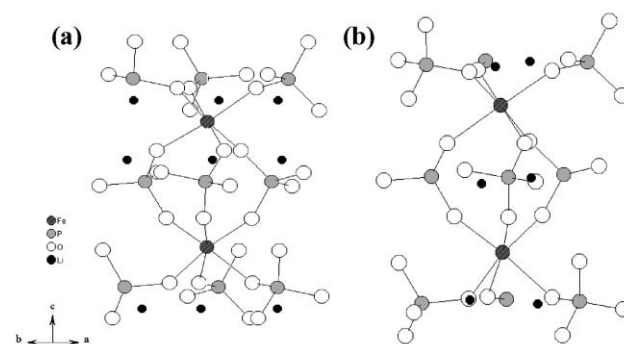
Both Li(1) and Li(2) take up in a fairly regular tetrahedral coordination with average <Li–O> distances 1.919 and 2.098 Å, respectively (Table 3). The small isotropic thermal parameter (1.0 Å<sup>2</sup>) indicates that both lithium ions are localized in the cavity as in the case of R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, although the mobility may be still higher than in the monoclinic phases, A-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.<sup>16</sup> The Li(2) atom has the same *z*-coordinate as the P atom (0.079). The lithium-ion layers are evenly spaced perpendicular to the *z*-direction (separation: 3.83 Å) unlike in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, where pairs of layers (separation: 2.25 Å) are separated from adjacent pairs by 5.39 Å (Fig. 4). These equally spaced layers of lithium ions enclose both M(1a) and M(1b) sites, compared to the pairs of lithium-ion layers in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, which only enclose M(1a) but not M(1b).<sup>12</sup> The Li<sup>+</sup> ions in R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> occupy two new Li(1) and Li(2) sites with occupancies 0.74(4) and 0.86(4), respectively. These give a total of 4.80(4) lithium atoms per formula unit, which agrees well with the value derived from our earlier Mössbauer study.<sup>17</sup> This neutron study would indicate the same higher Fe<sup>2+</sup> content as given by our Mössbauer spectroscopy, in contrast to the electrochemical value of 1.60 Li.

It has also been reported in our earlier study that there is a

**Fig. 4** Lithium ion distribution scheme in (a) R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and (b) R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, *x* = 1.8 Li.

slight preference for one of the Fe<sup>3+</sup> ions to be reduced before the other. This, in turn, implies that the extra lithium ions are located somewhat closer to one of the Fe ions. This is indeed supported here: the Fe(2)–Li(1) distance [2.29(6) Å] is much shorter than the Fe(2)–Li(2) distance [3.07(4) Å], while the distances from Fe(1) to the two lithium ions do not differ greatly. Since all oxygen atoms in the FeO<sub>6</sub> octahedra of R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> coordinate to lithium, all Fe–O distances are comparable. However, in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, where the lithium ions arrange in pairs of layers, Fe(1)–O(4) is longer [2.071(6) Å] than Fe(1)–O(1) [1.929(7) Å], since O(4) only participates in lithium coordination<sup>13</sup> (Fig. 5). The relatively large isotropic thermal displacement parameters seen for P, O(1), O(2) and O(3) would suggest disorder in the phosphate group, presumably resulting from vacancies in the arrangement of the lithium ions. The (PO<sub>4</sub>)<sup>3-</sup> tetrahedra in R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> are slightly distorted compared to those in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. This effect is clearly reflected in the <P–O> distances which are shorter in R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> than in R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.

It is interesting to speculate on the exceptionally large thermal displacement parameters for the PO<sub>4</sub> oxygens (Fig. 6). An obvious explanation would be that this is a result of systematic error in the powder data. This is most unlikely, however, since it only seems to affect selected atoms. Another possibility is superlattice formation involving Fe<sup>2+</sup>/Fe<sup>3+</sup> ordering along the *c*-direction. No evidence is found of superlattice reflections in this study, however. This could be related to an increase in Fe(1)–O1 distance as lithium ions rearrange during the reduction of Fe atoms from 3+ to 2+. In the average description of the R-Li<sub>5</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> structure, where all Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup>, the occupation factors for the two Li atoms would seem to tend towards 1 and 2/3.

**Fig. 5** The arrangement of Li ions in (a) R-Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and (b) R-Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.

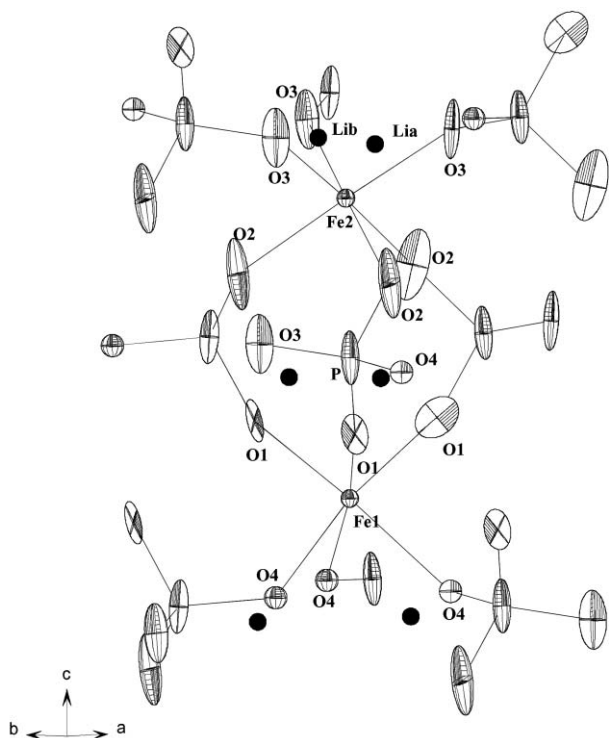


Fig. 6 The crystal structure of  $R\text{-Li}_{4.8}\text{Fe}_2(\text{PO}_4)_3$  perpendicular to the  $c$ -axis; thermal ellipsoids are drawn at 10% probability.

## Conclusion

The phase transformation of  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  into  $\text{Li}_5\text{Fe}_2(\text{PO}_4)_3$  proceeds through a rearrangement of lithium ions without greatly changing the  $[\text{Fe}_2(\text{PO}_4)_3]$  framework structure. From this study, it is difficult to assess whether this transformation leads to superlattice formation in the latter phase. However, the observed disorder affecting the  $\text{PO}_4$  group might well be an indication that different  $\text{PO}_4$  groups within the structure have different Li-ion environments. Future work will focus on single-crystal studies to see if a super-cell is formed, and on the electron distribution associated with the reduction of the Fe atoms.

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## References

- 1 A. Manthiram and J. B. Goodenough, *J. Power Sources*, 1989, **26**, 403.
- 2 Y. Takeda, K. Nakahara, M. Nishijima, N. Imanishi, O. Yamamoto, M. Takao and R. Kanno, *Mater. Res. Bull.*, 1994, **29**, 659.
- 3 K. S. Nanjundaswamy, A. K. Padhi, J. B. Goodenough, S. Okada, H. Ohtsuka, H. Arai and J. Yamaki, *Solid State Ionics*, 1996, **92**, 1.
- 4 A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 1188.
- 5 A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 1609.
- 6 C. Masquelier, A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Solid State Chem.*, 1998, **135**, 228.
- 7 J. B. Goodenough and V. Manivannan, *Denki Kagaku*, 1998, **66**, 1173.
- 8 A. S. Andersson, B. Kalska, L. Häggström and J. O. Thomas, *Solid State Ionics*, 2000, **130**, 41.
- 9 A. S. Andersson, J. O. Thomas, B. Kalska and L. Häggström, *Electrochem. Solid State Lett.*, 2000, **3**, 66.
- 10 S. Besner, Y. Choquette, J.-F. Magnan, F. Allaire, A. Vallée, E. Potvin, P. Hovington, N. Ravet and M. Armand, Abstract No. 204, 196th Electrochemical Soc. Meeting, 1999, Hawaii.
- 11 N. Ravet, J. B. Goodenough, S. Besner, M. Simoneau, P. Hovington and M. Armand, Abstract No. 127, 196th Electrochemical Soc. Meeting, 1999, Hawaii.
- 12 M. Pintard-Screpél, F. d'Yvoire and F. Rémy, *C. R. Acad. Sci. Paris*, 1978, **286**, 381.
- 13 C. Masquelier, C. Wurm, J. Rodriguez-Carvajal, J. Gaubicher and L. Nazar, *Chem. Mater.*, 2000, **12**, 525.
- 14 E. A. Genkina, L. A. Muradyan, B. A. Maksimov, B. Merinov and S. E. Sigarev, *Sov. Phys. Crystallogr.*, 1987, **32**(1), 40.
- 15 F. d'Yvoire, M. Pintard-Screpél, E. Bretey and M. de la Rochère, *Solid State Ionics*, 1983, **9–10**, 851.
- 16 C. Masquelier, J. Gaubicher and M. Querton, Abstract No. 220, 196th Electrochemical Soc. Meeting, 1999, Hawaii.
- 17 A. S. Andersson, B. Kalska, P. Eyob, D. Aerout, L. Häggström and J. O. Thomas, *Solid State Ionics*, 2001, **140**, 63.
- 18 Ö. Bergström, T. Gustafsson and J. O. Thomas, *J. Appl. Crystallogr.*, 1998, **31**, 103.
- 19 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
- 20 J. Rodriguez-Carvajal, *Physica B*, 1993, **192**, 55.
- 21 C. Delmas, A. Nadiri and J. L. Soubeyroux, *Solid State Ionics*, 1988, **28–30**, 419.