LiNi$_{0.66}$Fe$_{0.34}$PO$_4$

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Key indicators

Single-crystal X-ray study

T = 150 K

Mean σ(P–O) = 0.002 Å

Disorder in main residue

R factor = 0.020

wR factor = 0.043

Data-to-parameter ratio = 8.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Lithium nickel(II) iron(II) phosphate, LiNi$_{0.66}$Fe$_{0.34}$PO$_4$, was crystallized from an LiCl melt. The structure is closely related to the known phase LiFePO$_4$ but with mixed occupancy at the metal atom site of approximately 66% nickel and 34% iron. The Ni/Fe atom is octahedrally coordinated by six O atoms. The P atoms are tetrahedrally coordinated by four O atoms.

Comment

The solid-state phase LiFePO$_4$ was first structurally characterized by X-ray diffraction in 1938 (Björling & Westgren, 1938). However, the potential use of this olivine phase as a cathode material was not reported until 1997 (Padhi *et al.*, 1997). Currently, the material is the focus of research and development of lithium ion batteries. The late arrival of LiFePO$_4$ and related structures as candidates for possible cathode materials is primarily due to their low inherent electrical conductivity. Most prior scientific investigations were focused on materials with edge-shared transition metal octahedra, often exhibited in spinel structures (Tarascon & Armand, 2001). Transition metal oxides with edge-shared octahedra are more efficient ion conductors and tend to retain their structure better during reduction. Although LiFePO$_4$ contains both edge-shared and corner-shared polyhedra, marked increases in conductivity are observed by intercalating LiFePO$_4$ with multivalent cations such as Mg, Ti, W, and Al (Thackeray, 2002). A partially nickel-substituted compound,
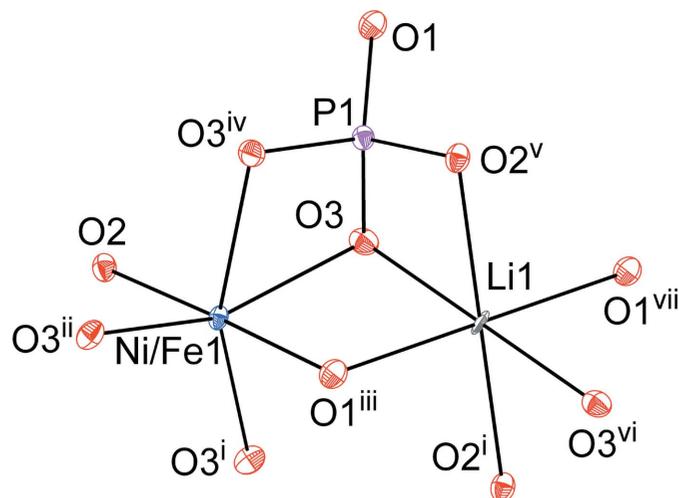
Figure 1
The asymmetric unit of LiNi$_{0.66}$Fe$_{0.34}$PO$_4$ with additional atoms to complete the coordination environments. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes (i) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$, (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$, (iii) $x, y, z - 1$, (iv) $x, -y + \frac{1}{2}, z$, (v) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$, (vi) $-x, -y, -z$, (vii) $-x, y - \frac{1}{2}, 1 - z$.]
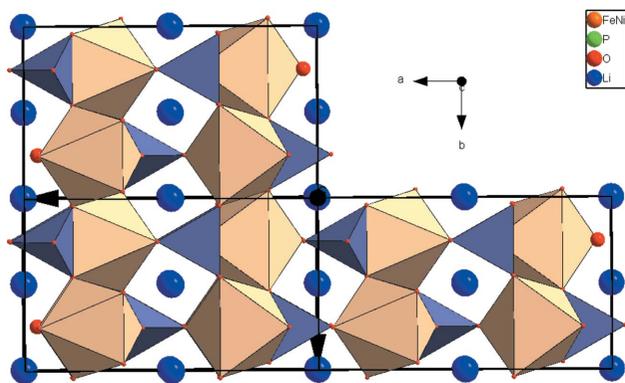
Figure 2
View, down the [010] direction, of the supercell contents. The unit cell is doubled along the a, b and c axes. The packing diagram illustrates the relationship between corner-shared and edge-shared polyhedra in the (110) plane.

$LiNi_{0.66}Fe_{0.34}PO_4$ has been characterized and its structure is presented here.

The title compound is isostructural with $LiFePO_4$. It features MO_6 octahedra (M = Fe, Ni) and PO_4 tetrahedra that form alternating 'chains' of corner-sharing and edge-sharing polyhedra along the [100] and [001] directions. Conversely, in the (010) plane there is a discrete layer of edge-sharing polyhedra followed by a discrete layer of corner-sharing polyhedra as one moves down the [100] axis. Lithium cations reside in the cavities between the polyhedra, yielding LiO_6 octahedra. Approximately 66 (4)% of the metal-atom sites in the structure are occupied by Ni, which is somewhat lower than the 80 mol-% in the starting mixture. In the flux growth, the chemical reaction of the $NiCl_2$ in certain portions of the starting mixture might not be fully completed, resulting in an Ni concentration in the analyzed crystal which is different from that in the starting mixture.

The MO_6 octahedra are severely distorted [cis-O—Ni—O angles between 68.53 (8)° and 114.22 (9)°]. Even the LiO_6 octahedra are rather distorted [cis-O—Li—O 71.82 (7)°– 108.18 (7)°]. Similar distortions, albeit to a lesser extent, are observed in the PO_4 tetrahedra, with angles in the range 102.69 (2)°–113.90 (8)°·The site occupation factors of Fe and Ni were refined with the constraint $x_{Ni} = 1 - x_{Fe}$.

Experimental

Synthesis: $LiNi_{0.66}Fe_{0.34}PO_4$ single crystals were grown in sealed platinum crucibles by standard flux-growth techniques with LiCl as the flux. High purity $FeCl_2$ (99.999% Aldrich), $NiCl_2$ (99.999% Aldrich) and Li_3PO_4 (99.999% Aldrich) powders were mixed with a molar ratio of 1:4:5. A small hole of about 50 μm diameter was drilled in the crucible to release the pressure from the high vapor pressure of LiCl. The mixture was pre-melted at 800 K for 2 h, heated to 890 K over 5 h, soaked at 890 K for 10 h, slowly cooled to 710 K at a rate of 0.7 K h^{-1} and then further cooled to 650 K at 1.5 K h^{-1}. The furnace was turned off at 650 K. The crystals were extracted from the mixture by dissolving the extra LiCl with water at room temperature. The crystal used for the diffraction measurement in this study has a dark

red–brown color and a volume of about 0.1 mm^3. Powder X-ray diffraction of the crushed single crystals revealed a single-phase product.

Crystal data

$LiNi_{0.66}Fe_{0.34}PO_4$	$V = 277.91$ (8) Å^3
$M_r = 159.63$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 10.0871$ (16) Å	$\mu = 6.84$ mm^{-1}
$b = 5.8845$ (10) Å	$T = 150$ (2) K
$c = 4.6820$ (8) Å	$0.19 \times 0.18 \times 0.14$ mm

Data collection

Rigaku SCXmini diffractometer	2026 measured reflections
Absorption correction: multi-scan	345 independent reflections
(*ABSCOR*; Higashi, 1995)	328 reflections with $I > 2\sigma(I)$
$T_{min} = 0.568$, $T_{max} = 0.692$	$R_{int} = 0.033$
(expected range = 0.309–0.376)	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	43 parameters
$wR(F^2) = 0.044$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$S = 1.18$	$\Delta\rho_{min} = -0.47$ e Å^{-3}
345 reflections	

Table 1
Selected bond lengths (Å).

Ni1—O2	2.051 (2)	P1—O2^{iv}	1.538 (2)
Ni1—O3^{i}	2.0557 (15)	P1—O3^{iii}	1.5572 (16)
Ni1—O1^{ii}	2.111 (3)	Li1—O2^{iv}	2.0844 (15)
Ni1—O3^{iii}	2.1599 (15)	Li1—O3^{v}	2.1327 (15)
P1—O1	1.523 (2)	Li1—O1^{vi}	2.1464 (16)

Symmetry codes: (i) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (ii) $x, y, z-1$; (iii) $x, -y+\frac{1}{2}, z$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x, -y, -z$; (vi) $-x, -y, -z+1$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *SCXmini Benchtop Crystallography System Software* (Rigaku, 2006); data reduction: *CrystalStructure* (Rigaku, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SCXmini Benchtop Crystallography System Software*; software used to prepare material for publication: *CrystalStructure*.

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