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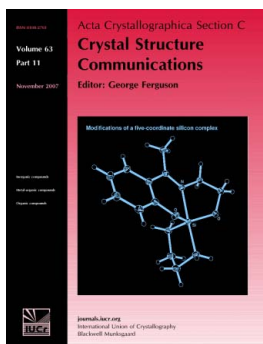
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Li_{0.97}Fe^{II}_{0.79}Fe^{III}_{0.15}(PO₄), a new oxidized triphylite-type phosphate

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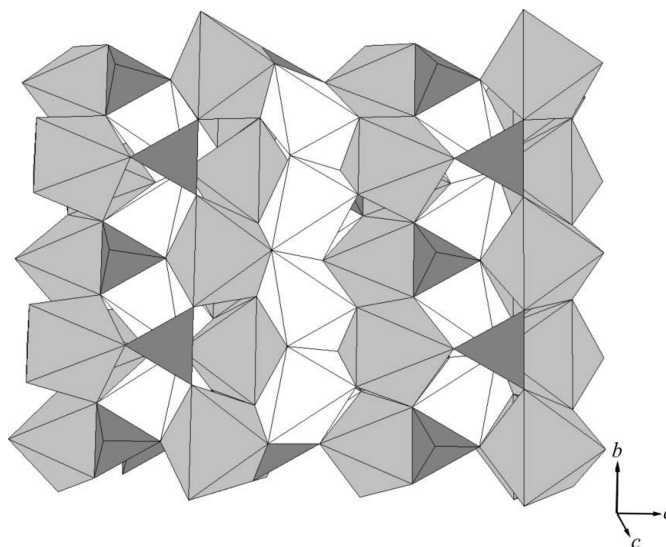
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This paper reports a new partially oxidized triphylite-type phosphate (lithium iron phosphate), which has been synthesized hydrothermally at 973 K and 0.1 GPa. The structure is similar to that of natural triphylite, LiFe(PO₄), and is characterized by two chains of edge-sharing octahedra parallel to the *b* axis. The weakly distorted *M1* octahedra contain Li atoms, whereas the more strongly distorted *M2* octahedra contain Fe^{II} and Fe^{III} atoms. Refined site occupancies and bond-valence analysis show the presence of Fe^{III} and vacancies on the *M2* site, mainly explained by the substitution mechanism $3 \text{Fe}^{\text{II}} = 2 \text{Fe}^{\text{III}} + \text{vacancies}$.

Comment

Triphylite [Li(Fe,Mn)PO₄, *a* = 4.690, *b* = 10.286, *c* = 5.987 Å, space group *Pbnm*; Losey *et al.*, 2004] is an accessory phosphate mineral occurring in granitic pegmatites, where it forms a solid solution with lithiophilite [Li(Mn,Fe)PO₄]. The crystal structure of these phosphates, which are isostructural with minerals of the olivine group, has been investigated from synthetic samples (Geller & Durand, 1960; Yakubovich *et al.*, 1977) and natural minerals (Finger & Rapp, 1969; Losey *et al.*, 2004; Fehr *et al.*, 2007; Hatert *et al.*, 2012). Since Padhi *et al.* (1997) reported the reversible electrochemical extraction of lithium from LiFePO₄, the olivine-type phosphates LiMPO₄ (*M* is Fe, Mn, Co or Ni) have received much attention as candidates for lithium batteries. The number of publications devoted to these compounds has increased linearly since 2001 and reached 300 publications per year in 2010. Recently, Kang & Ceder (2009) showed that LiFePO₄-based batteries can achieve ultrafast charging and discharging in 10–20 s, thus reaching the performance of supercapacitors. These features make LiFePO₄ the best candidate for producing batteries for many applications, such as electric bicycles, boats or cars, or for the storage of green energy.

This increasing interest in lithium iron phosphates prompted us to investigate the Li–Fe^{II}–Fe^{III} (+PO₄) system in detail using hydrothermal techniques, at temperatures between 400 and 973 K and under a pressure of 0.1 GPa (Dal Bo, 2011). In an experiment performed at 973 K (H.359), we

**Figure 1**

The crystal structure of Li_{0.97}Fe^{II}_{0.79}Fe^{III}_{0.15}(PO₄). Key: *M1*O₆ octahedra are white, *M2*O₆ octahedra are light grey and PO₄ tetrahedra are dark grey.

observed black crystals which gave an X-ray powder diffraction pattern similar to that of triphylite. A single-crystal structure determination confirmed this hypothesis and indicated the presence of vacancies on both cationic sites of the structure, and of significant amounts of Fe^{III} on the *M2* site. The present paper reports the crystal structure of this new partially oxidized triphylite-type phosphate, Li_{0.97}Fe^{II}_{0.79}Fe^{III}_{0.15}(PO₄).

The structure of Li_{0.97}Fe^{II}_{0.79}Fe^{III}_{0.15}(PO₄) was refined in the space group *Pnma* (No. 62) and is similar to those of natural triphylite-type phosphates. It is characterized by two chains of edge-sharing octahedra parallel to the *b* axis (Fig. 1). The first chain contains weakly distorted *M1* octahedra occupied by Li atoms [Li–O = 2.0900 (13)–2.1872 (13) Å], whereas the second chain contains more strongly distorted *M2* octahedra occupied by Fe atoms [Fe–O = 2.0630 (13)–2.2456 (14) Å]. The chains are connected in the *a* direction by sharing edges of their octahedral sites, and the resulting planes are connected in the *c* direction by the PO₄ tetrahedra.

Refinement of the site-occupancy factors on the crystallographic sites of Li_{0.97}Fe^{II}_{0.79}Fe^{III}_{0.15}(PO₄) showed that vacancies occur on both the *M1* and *M2* sites, which are occupied by 0.97 (3) Li and 0.935 (4) Fe, respectively. The charge deficit induced by these vacancies is compensated by a partial oxidation of Fe on the *M2* site; charge transfers between Fe^{II} and Fe^{III} on that site explain the black colour of the phosphate. The substitution mechanism responsible for 80% of the Fe^{III} insertion in the *M2* site corresponds to $3 \text{Fe}^{\text{II}} = 2 \text{Fe}^{\text{III}} + \text{vacancies}$ and expresses an increasing high-temperature miscibility towards Li₃Fe^{III}₂(PO₄)₃ (Masquelier *et al.*, 1998). The minor substitution mechanism, responsible for the insertion of 20% of Fe^{III} in the structure, is $\text{Li}^+ + \text{Fe}^{\text{II}} = \text{vacancies} + \text{Fe}^{\text{III}}$; this mechanism has been widely described in natural and synthetic triphylite-type phosphates (Quensel, 1937; Mason, 1941; Padhi *et al.*, 1997; Andersson *et al.*, 2000).

The final site populations, calculated from the observed site occupancies and assuming charge balance, are 0.97 Li + 0.03 vacancies on *M1*, and 0.79 Fe^{II} + 0.15 Fe^{III} + 0.06 vacancies on *M2*. In order to confirm these site populations, bond-valence sums were calculated using the empirical parameters of Brown & Altermatt (1985). The P1 bond-valence sum is 4.91. The Li1 bond-valence sum is 0.95, in good agreement with the 0.97 Li atoms observed on the *M1* site. The Fe2 bond-valence sum of 2.01 is very close to the ideal value of 2.03, calculated from the *M2* site populations described above.

Experimental

The title compound was synthesized under hydrothermal conditions. The starting material was prepared by mixing Li₃PO₄, FePO₄ and Fe in a 4:2:1 molar ratio, and by then homogenizing this mixture in an agate mortar. A small quantity of the mixture (about 25 mg) was sealed in a gold tube with an outer diameter of 2 mm and a length of 25 mm, containing distilled water (2 mg). The gold capsule was then inserted in a Tuttle-type pressure vessel (Tuttle, 1949) and maintained at a temperature of 973 K and a pressure of 0.1 GPa. After 7 d, the gold tube containing the sample was quenched in the autoclave to room temperature in a stream of cold air. The synthesized products were identified by X-ray powder diffraction (PANalytical PW-3710 goniometer using Fe K α radiation, $\lambda = 1.9373 \text{ \AA}$); they consisted of black crystals of the title compound, associated with colourless Li₃PO₄ crystals.

A chemical analysis was performed using a CAMEBAX SX-100 electron microprobe (15 kV acceleration voltage, 5 nA beam current, analyst T. Theye, Stuttgart, Germany). The standard used to calibrate both Fe and P was graffonite from Kabira (sample KF16, Fransolet, 1975). The average of 11 point analyses gives P₂O₅ 46.30, Fe₂O₃* 13.24, FeO* 29.00 and Li₂O* 9.75, total 98.29 wt. % (* denotes values calculated to maintain charge balance, assuming one Li atom per formula unit). The chemical composition, calculated on the basis of one P atom per formula unit, corresponds to Li_{1.00}Fe^{II}_{0.62}Fe^{III}_{0.25}(PO₄), in fairly good agreement with the composition calculated from the structural data, Li_{0.97}Fe^{II}_{0.79}Fe^{III}_{0.15}(PO₄).

Crystal data

LiFe ^{II} _{0.619} Fe ^{III} _{0.254} (PO ₄)	$V = 290.38 (2) \text{ \AA}^3$
$M_r = 615.69$	$Z = 1$
Orthorhombic, <i>Pnma</i>	Mo K α radiation
$a = 10.3060 (4) \text{ \AA}$	$\mu = 5.22 \text{ mm}^{-1}$
$b = 6.0041 (2) \text{ \AA}$	$T = 293 \text{ K}$
$c = 4.69281 (15) \text{ \AA}$	$0.15 \times 0.10 \times 0.08 \text{ mm}$

Data collection

Agilent Xcalibur Eos diffractometer	5358 measured reflections
Absorption correction: analytical	545 independent reflections
[<i>CrysAlis PRO</i> (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]	$R_{\text{int}} = 0.041$
$T_{\text{min}} = 0.595$, $T_{\text{max}} = 0.751$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	42 parameters
$wR(F^2) = 0.072$	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
$S = 1.20$	$\Delta\rho_{\text{min}} = -1.26 \text{ e \AA}^{-3}$
545 reflections	

All atoms were refined anisotropically. The refined site-occupancy factors then indicated low electronic densities on the *M1* and *M2* sites, thus showing that these sites were not fully occupied by Li and Fe, respectively. Consequently, Li and vacancies were refined on the *M1* site, whereas Fe and vacancies were refined on the *M2* site.

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 1993); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3107). Services for accessing these data are described at the back of the journal.

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