

Gaining Insights into the Energetics of FePO₄ Polymorphs[†]

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The energetic stability of FePO₄ polymorphs (berlinite, heterosite, monoclinic, and high-pressure forms) is investigated combining first-principles and experimental methods. Calculations at the density functional theory (DFT and DFT+U) level performed using the local density approximation (LDA) and the generalized gradient approximation (GGA and GGA+U) yield different relative energetic stability for those forms of iron phosphate. To discern the appropriate computational methodology, we have measured the transport and magnetic properties of high pressure (HP)-FePO₄; we found that it is an insulating compound with a room-temperature resistivity of 2.10⁷ Ohm.cm, and Fe³⁺ ions in high spin configuration ($t_{2g}^2e_g^3$). Both LDA and GGA methods fail to reproduce the physical properties of HP-FePO₄, which are well-predicted within the GGA+U framework. This method predicts that berlinite-FePO₄ is the most stable form at ambient pressure, whereas HP-FePO₄ is the stable form at pressures above 2 GPa. Heterosite and monoclinic FePO₄ are predicted as metastable phases in the whole pressure range. Accordingly, we found that both monoclinic and berlinite transform to HP-FePO₄ under pressure (pressure range 2–6 GPa, 900 °C). Differential thermal analysis (DTA) and temperature-XRD measurements reveal that HP-FePO₄ reverts exothermically and irreversibly to the berlinite form at about 700 °C. Discrepancies of our combined experimental-computational results with a previous high-temperature oxide melt solution calorimetry investigation are discussed.

Introduction

The good performance of olivine-LiFePO₄ as positive electrode material for lithium ion batteries¹ points toward other FePO₄ crystalline forms as potential electrode materials. Five polymorphs of anhydrous FePO₄ are known to exist at room temperature: one obtained by delithiation of olivine-LiFePO₄,^{2,3} which is related to the mineral heterosite (Fe_{0.65}Mn_{0.35}(PO₄)⁴), a second form isostructural with the mineral berlinite (AlPO₄) and the α -quartz-SiO₂,⁵ a monoclinic and an orthorhombic forms both prepared dehydrating precursors obtained by hydrothermal procedures,⁶ and finally a high-pressure modification crystallizing with the CrVO₄-type structure

(hereafter HP-FePO₄).⁷ Figure 1 shows schematic representations of the four polymorphs of FePO₄ we have considered in this work. In the berlinite structure, each iron and phosphorous atom is four-fold coordinated to oxygen atoms in a tetrahedral environment. In both the monoclinic and orthorhombic forms, Fe³⁺ is tetracoordinated as well. This tetrahedral coordination has been identified as a handicap for effective lithium insertion–deinsertion.^{8,9} In the heterosite and HP forms, the Fe³⁺ ions are in an octahedral environment. However, a poor lithium mobility precludes the utilization of the HP-form as electrode in lithium batteries.^{10,11} Though the crystallography and electrochemical properties of each polymorph has been reported, their relative thermodynamic stability remains as a controversial point. Solving this issue could open new perspectives to prepare novel polymorphs with potential applications in lithium batteries.

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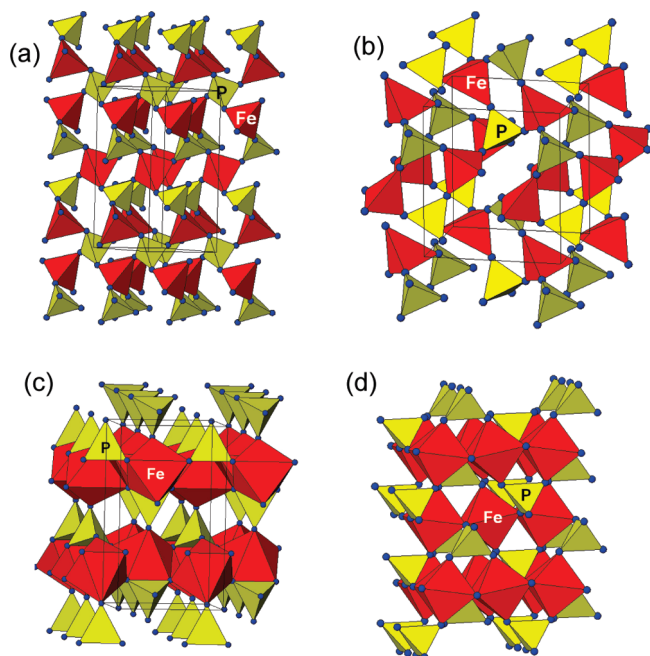


Figure 1. Schematic structures of the FePO_4 polymorphs under investigation: (a) berlinite, (b) monoclinic, (c) heterosite, and (d) HP- FePO_4 .

Berlinite- FePO_4 is the most common form of FePO_4 , and it has been considered as the most stable form of FePO_4 for a long time. As reported by Song et al.,⁶ the monoclinic and orthorhombic varieties of FePO_4 transform irreversibly to the berlinite form at 450 °C. A transformation of heterosite- FePO_4 to the berlinite phase was observed in the Differential Thermal Analysis (DTA) beginning at around 580 °C¹² and in the differential scanning calorimetry (DSC) at 700 °C.¹³ This phase transformation was not reversed on cooling, suggesting that the berlinite form may be the thermodynamically stable phase.¹² However, high-temperature oxide melt solution calorimetry measurements indicate that at 25 °C heterosite is 12 kJ/mol more stable than berlinite.¹³ To add more controversy, a computational investigation at the density functional theory (DFT) level yields quite different stability depending on the exchange-correlation functional.¹⁴ For the local density approximation (LDA) calculations, the ordering from the most to least stable structures is HP, monoclinic, heterosite, and berlinite. Within the generalized gradient approximation (GGA), the reported sequence of stability is: berlinite, monoclinic, heterosite, and HP. Namely, according to DFT, the heterosite form is the third in stability out of the four polymorphs. Interestingly, in the same work, a metallic behavior is predicted for the HP- FePO_4 form. In this context, and to validate the suitability of the LDA/GGA method to investigate these polymorphs, an experimental study of the thermal stability (and eventual transformation to other FePO_4 varieties) and electrical properties of HP- FePO_4 is desirable.

Aiming to gain more insight into the various FePO_4 polymorphs, in this work we have prepared and characterized HP- FePO_4 by means of DTA, magnetometry, and electrical transport measurements. Computational methods at the DFT level have been applied to investigate the four FePO_4 polymorphs shown in Figure 1. Extending the previous DFT investigation to the DFT+U method, we will show that the physical properties (electrical and magnetic) of HP- FePO_4 can only be reproduced when a Hubbard like-term (U) is introduced in the calculation. The relative stability of polymorphs is then analyzed combining the GGA+U calculations and experimental methods; in particular, we focus on the effect of pressure over these structures, because the coordination around Fe^{3+} ions can be tuned by the synthesis pressure, and the electronic conductivity improved.

Methodology

Experimental Section. Monoclinic- FePO_4 was prepared as previously reported by Song et al.⁶ Although berlinite- FePO_4 is commercially available (Merck), high-crystalline samples were prepared by heating stoichiometric amounts of high-purity $(\text{NH}_4)_2\text{HPO}_4$ (Merck) and Fe_2O_3 (Merck) at 900 °C for 24 h.¹⁵ To obtain the HP- FePO_4 polymorph, either the berlinite or monoclinic phases were treated at pressures ranging from 0.4 GPa to 6 GPa and 900 °C in a belt-type press. The vessel is first pressurized, and then both pressure and temperature are applied for 1 hour, followed by quenching to ambient conditions.

Once HP- FePO_4 was obtained, its phase transition back to the ambient pressure polymorph was analyzed by differential thermal analysis (DTA) using a Netzsch STA 409 PC Luxx apparatus between RT and 800 °C. The heating rate was 10 °C/min to 800 °C and nitrogen was used as purge gas.

All the samples were characterized by X-ray powder diffraction performed on a Bruker D8 high-resolution X-ray powder diffractometer, using monochromatic $\text{CuK}\alpha_1$ ($\lambda = 1.5406$ Å) radiation obtained with a germanium primary monochromator, and equipped with a position sensitive detector (PSD) MBraun PSD-50M. The treatment of the diffraction data was carried out by the Rietveld method using the FullProf program.¹⁶ High-temperature powder XRD data at air were carried out on a Panalytical X'PERT PRO diffractometer operating in a θ/θ configuration supplied with a X'Celerator fast detector and Ni K- β -filter with Cu K α radiation and a high-temperature Anton Paar HTK1200 camera. Heating rate was 50 °C per hour from RT to 800 °C, and patterns were collected between 10 and 70° 2 θ with a step size of 0.035 and counting time of 200 s.

For transport measurements, berlinite- FePO_4 powder was conformed into 13 mm diameter pellets by uniaxially applying a pressure of 0.37 kbar and sintering for 12 h at 650 °C. Pelletized HP- FePO_4 was used as obtained from the Belt-type press. DC transport measurements in the temperature region 160 K < T < 280 K have been done in 2-contact configuration using Keithley sourcemeter K2410. Magnetic properties of HP- FePO_4 have been studied by using a Quantum Design SQUID magnetometer; the measurements being performed in a magnetic field of 0.01 Tesla.

Computational. The total energy of FePO_4 was calculated using the DFT and DFT+U methods as implemented in the

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Vienna ab initio simulation package (VASP).^{17,18} Tang et al.¹⁴ conducted a detailed investigation of the stability of FePO₄ polymorphs within the DFT framework with the exchange-correlation energy approximated in the generalized gradient approximation (GGA) and in the localized density approximation (LDA). They utilized two set of potentials; ultrasoft-pseudopotential (PP), and projector augmented wave (PAW).¹⁹ In addition, they performed calculation based on the linear augmented wave method (LAPW). In the present work we have restricted the DFT calculations to the computationally less expensive PP-LDA and PP-GGA methods. We will demonstrate both LDA and GGA are inadequate to capture the physics of this system. Thus, in a second approach, total energies were calculated within the DFT+U framework. Projector augmented wave (PAW) potential sets¹⁹ were used with the exchange and correlation energies approximated in the generalized gradient approximation with the Hubbard parameter correction (GGA+U) following the rotationally invariant form.^{18,20} Within this approach, the onsite Coulomb term U and the exchange term J can be grouped together into a single effective parameter ($U-J$) and this effective parameter will be simply referred as U in this paper. A value of $U = 4.5$ eV was used for FePO₄ polymorphs, as this has been reported to be an appropriate value for Li_xFePO₄.^{10,21,22} This is quite close to the U value of 4.3 eV extracted from self-consistent calculations for the olivine-Li_xFePO₄ system.²¹ For the exchange and correlation functional, we chose two different forms suggested by Perdew et al: PBE²³ and PW91.²⁴ A good analysis of the nonequivalence between both functionals is provided in ref 25. For completeness, calculations were also performed using the PBE potentials with $U = 2$ eV. In all cases, a ferromagnetic configuration was used to define the initial ground state. The energy cut off for the plane wave basis set was kept fix at a constant value of 500 eV throughout the calculations. The reciprocal space sampling was done with k -point grids of $4 \times 6 \times 6$ for heterosite, monoclinic, and berlinite varieties and $6 \times 6 \times 6$ for the primitive cell of HP-FePO₄. As a first step, the structures were fully relaxed (cell parameters, volume and atomic positions); the final energies of the optimized geometries were recalculated so as to correct the changes in the basis set of the wave functions during relaxation. Secondly, from the relaxed structure within the GGA+U approximation, calculations were performed at various constant volumes and the energy–volume data were fitted to the Murnaghan equation of state.²⁶

$$E(V) = B_0 V_0 \left[\frac{1}{B'(B'-1)} \left(\frac{V_0}{V} \right)^{(B'-1)} + \frac{V}{B'V_0} - \frac{1}{(B'-1)} \right] + E_0 \quad (1)$$

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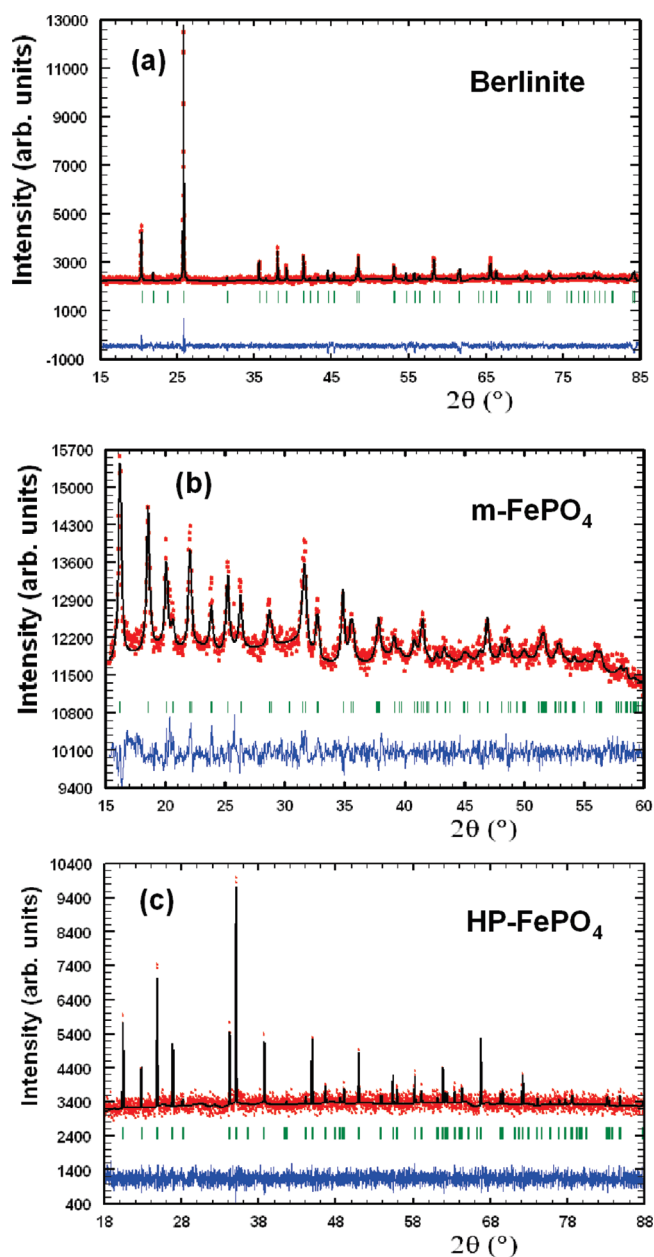


Figure 2. Profile refinement of XRD patterns of (a) berlinite-FePO₄, (b) monoclinic-FePO₄, and (c) the HP-FePO₄ sample used for physical measurements (prepared at 4 GPa and 900 °C). Observed (circles), calculated (solid line), and their difference (blue line). The Bragg reflection positions are indicated by vertical bars.

where B_0 is the bulk modulus at zero pressure, B' its first derivative with respect to pressure, E_0 the minimum energy, and V_0 the volume at the minimum of energy.

Results and Discussion

Synthesis and Structural Characterization of FePO₄ Polymorphs. The XRD pattern of the starting berlinite and monoclinic polymorphs are shown in panels a and b in Figure 2. Both forms display the same behavior under HP/HT treatment. For pressures between 2 and 6 GPa (temperature 900 °C) they transform into the HP-FePO₄ phase. However, a less-crystalline HP-FePO₄ is obtained when starting from the monoclinic phase. The XRD pattern of the HP sample used for physical

Table 1. Experimental Cell Parameters and Agreement Factors for FePO₄ Polymorphs

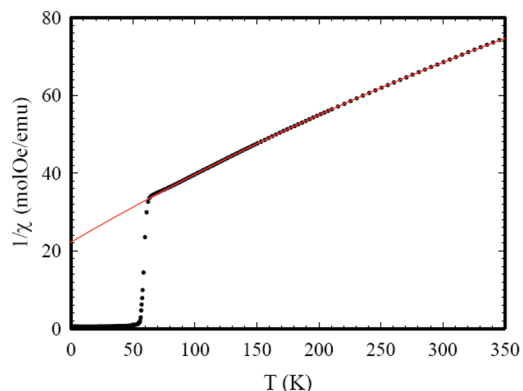
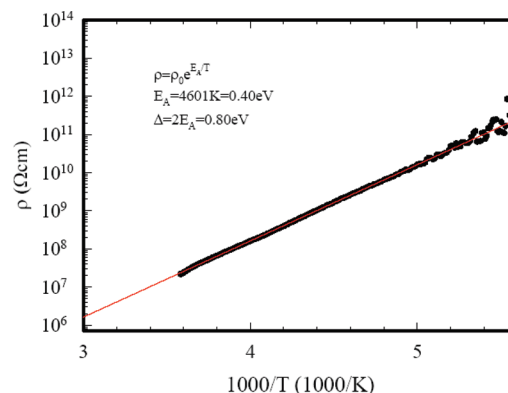
	FePO ₄ Polymorph		
	berlinite	monoclinic	HP
<i>a</i> (Å)	5.0338(2)	5.489(1)	5.2238(2)
<i>b</i> (Å)		7.475(3)	7.7736(3)
<i>c</i> (Å)	11.2463(6)	8.054(3)	6.3276(2)
β (deg)		96.01(2)	
<i>V</i> (Å ³)	246.80(2)	328.6(2)	256.95(2)
S.G.	<i>P</i> 3 ₁ 21	<i>P</i> 2 ₁ / <i>n</i>	<i>Cmcm</i>
<i>R</i> _{Bragg}	0.15	0.47	0.03
<i>R</i> _{wp}	0.027	0.29	0.04
<i>R</i> _{exp}	0.021	0.23	0.017
χ^2	1.74	1.72	5.34

characterization (prepared from berlinite at 4 GPa) is shown in Figure 2c. Table 1 summarizes the refined cell parameters for the prepared polymorphs together with agreement factors. All these parameters are in good agreement with previous values, see ref 6 for berlinite, ref 7 for monoclinic-FePO₄ and refs 8 and 11 for the HP-polymorph. Noteworthy, transformation of berlinite or monoclinic form to the HP form was not accomplished in HP/HT experiments performed at 1 and 0.4 GPa (900 °C).

Physical Characterization of HP-FePO₄. Figure 3 shows the magnetic susceptibility measured in a field cooling (FC). A transition at about 57 K is clearly seen, which is in agreement with the previously reported ordering temperature of HP-FePO₄ (60 K in ref 14). From the paramagnetic region (between 100 K and 350 K) a magnetic moment of 6.06(6) Bohr's magnetons (BM) and a Curie-Weiss temperature of -110(1) K were obtained. The uncertainties (in brackets) are based on the following criterion: the nominal value refers to the minimum residual in a least-square fit. If these values are shifted by the number in brackets and all other fit parameters are re-refined, a 10% higher residual than the minimum is obtained. Thus, there is not the slightest doubt that Fe is in its normal +3 high-spin state (*t*_{2g}³ *e*_g²).

The room-temperature resistivity of HP-FePO₄ is ρ_{RT} 2×10^7 Ohm cm. This value is at least six orders of magnitude smaller than that of berlinite. The latter material is insulating and its resistance too high to be experimentally determined; the resistivity is estimated to be higher than 4×10^{13} Ohm cm, which is our experimental detection limit. The electrical transport of HP-FePO₄ is thermally activated (Figure 4) with an activation energy of $E_A = 0.40$ eV, indicating the "transport" energy gap of $\Delta = 2E_A = 0.80$ eV.

DFT vs DFT+U Calculations of HP-FePO₄. Table 2 compares the calculated lattice parameters for the fully relaxed structures of HP-FePO₄ (PP-LDA, PP-GGA, PBE-GGA+U (*U* = 4.5 eV), PBE-GGA+U (*U* = 2 eV) and PW91-GGA+U (*U* = 4.5 eV) with the experimental ones. It may be concluded that all calculation methods allow a correct prediction of the cell parameters, with differences around 3%, which is typical for the state-of-the-art

**Figure 3.** SQUID magnetometry data for HP-FePO₄ in an applied field of 0.01 T.**Figure 4.** Resistivity of HP-FePO₄ versus inverse temperature. Black line is a fit to $\rho = \rho_0 \exp(E_A/kT)$.

approximations to density functional theory in transition metal phosphates.^{21,27}

Table 2 lists the band gaps values extracted from the calculated density of state (DOS). Figure 5 shows the calculated density of states (DOS) of HP-FePO₄, with the partial DOS of Fe represented in blue. To easily discuss the results, we have arbitrarily chosen the Fermi level as the origin of the energy. Within the PP-LDA approximation, a metallic behaviour is predicted. Furthermore, the calculated magnetic moment, with each unpaired electron contributing one Bohr magneton, is only 4.5 BM per formula unit. Thus, LDA fails to reproduce both the magnetic and electrical properties of HP-FePO₄. As shown in Figure 5 the PP-GGA predicts a metallic character for HP-FePO₄. These results fully agree with those reported by Tang et al.,¹² who in addition extended their computational DFT investigation to the PAW-LDA/GGA and LAPW-LDA/GGA methods. Clearly, the disagreement with experiments can not be corrected by the choice of the potential set utilized in the GGA/LDA calculations.

Figure 5 shows that the insulating character of HP-FePO₄ is well predicted only within the GGA+U approximation since in the DOS the Fermi level resides in the gap between the valence and conduction bands. Predicted band gaps are 0.53 eV for PBE-GGA+U, *U* = 2 eV and 1.38 eV for PBE-GGA+U, *U* = 4.5 eV, the latter *U* value being more appropriate according to previous

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Table 2. Calculated Lattice Parameters (\AA), Volume (\AA^3), and Band-Gap (eV) for HP-FePO₄ Polymorphs Calculated within the DFT and DFT+U Methods

	PP- LDA	PP- GGA	PBE-GGA+U (2 eV)	PBE-GGA+U (4.5 eV)	PW91-GGA+U (4.5 eV)	experimental
a (\AA)	5.231	5.293	5.303	5.265	5.271	5.2238(2)
b (\AA)	7.727	7.933	7.910	7.906	7.909	7.7736(3)
c (\AA)	6.154	6.508	6.441	6.434	6.429	6.3276(3)
V (\AA^3)	248.74	273.26	270.16	267.76	268.20	256.95(2)
band gap (eV)	metal	metal	0.53	1.38	1.36	0.8

Table 3. Ground State Volume (V , \AA^3) and Relative Energy Difference (E , eV/f.u.) for FePO₄ Polymorphs Calculated within the DFT and DFT+U Methods

FePO ₄ -polymorph	PP-LDA		PP-GGA		PBE-GGA+U (2 eV)		PBE-GGA+U (4.5 eV)		PW91-GGA+U (4.5 eV)		experimental volume (\AA^3)
	V	E	V	E	V	E	V	E	V	E	
berlinite	82.55	0.171	90.81	0	87.58	0	90.81	0	87.68	0	82.27 ^a
monoclinic	81.60	0.077	86.81	0.084	86.40	0.089	86.255	0.061	85.95	0.033	82.15 ^a
heterosite	68.31	0.104	73.23	0.244	72.46	0.225	71.89	0.148	71.88	0.133	68.25 ³⁴
HP	62.18	0	68.31	0.297	67.54	0.275	66.985	0.174	67.05	0.157	64.23 ^a

^a This work.

reports.^{10,21,22} The DOS calculated within the PW91-GGA+U $U = 4.5$ eV also yields a gap of 1.36 eV. Differences between the “transport” gap extracted from the DC measurements (0.80 eV) and the GGA+U-calculated one (1.38 eV for $U = 4.5$ eV) suggests the occurrence in the material of an electronic conduction mechanism added to the thermal excitations of electrons. Indeed, in olivine-Li_xFePO₄ the conduction is by polarons,¹⁹ the conductivity being mainly determined by the electron (or hole) mobility. As seen in Figure 5, within the GGA+U, Fe⁺³ ions are in the high spin configuration with the spin-down band totally unoccupied. The calculated magnetic moment (5 BM per formula unit) corresponds to five unpaired electrons for the Fe centres ($t_{2g}^3 e_g^2$ configuration), in good agreement with the experiments. In short, DFT reproduces the physical properties of HP-FePO₄ only when a Hubbard-like term is introduced in the calculation.

Phase Stability. Table 3 summarizes the energy and volume obtained for each FePO₄ form within the DFT and DFT+U frameworks. The relative energy of the polymorphs depends on the choice of the functional (GGA or LDA). Our results within the PP-GGA and PP-LDA are consistent with those previously reported.¹⁴ That investigation demonstrated that the relative stability is independent of the potential set utilized (PP, PAW or LAPW). Within the LDA, the most stable form is the HP-FePO₄, a phase whose obtainment requires HT/HP treatment. On the contrary, berlinite that can be produced by simple chemical reactions is predicted to be the most unstable form. Obviously, the LDA result contradicts many fundamental experimental observations. Within the PAW-GGA+U (either PBE or PW91) and the GGA, the ordering of the most stable to least stable structures is the same; berlinite, monoclinic, heterosite, and HP. This sequence is in principle in logical agreement with the synthetic routes known to result in the specific polymorphs. The heterosite form is the third out of four in stability, which is not surprising keeping in mind that this form can only be prepared by chemical delithiation of olivine-LiFePO₄. Chemical delithiation is a well-known

soft-chemistry method to produce metastable phases which are not obtainable by other means. We have proven that GGA/LDA fails to reproduce the physical properties of HP-FePO₄, and therefore relative energies extracted from GGA+U calculations are the only reliable. Because minor differences are observed between the PBE and PW91, we chose the PBE-GGA+U ($U = 4.5$ eV), which is most widely used. Hence, the berlinite form is predicted as the most stable one, with an energy difference of 0.15 and 0.18 eV/f.u. compared to heterosite and HP structures, respectively.

With the FePO₄ polymorphs possessing different densities and Fe-coordination polyhedra, pressure is an interesting parameter to be investigated (pressure favors denser phases and high coordination number). Besides the existence of the high-pressure polymorph, several hydrated varieties can be isolated under hydrothermal conditions,^{6,28} evidencing a rich polymorphism for FePO₄ as a function of pressure. Pressure is an easy parameter for DFT investigations; the stability of a given FePO₄ form as a function of pressure can be extracted from a series of total energy calculations at constant volume that are subsequently fitted to an equation of state. Table 4 reports the parameters of the Murnaghan equation of state fitted to the ab initio Energy (Volume) data for the investigated FePO₄ forms (PBE-GGA+U, $U = 4.5$ eV), and the extracted density value compared to the experimental ones. Generally speaking, there is a fair agreement between experiments and calculations (calculated $B_{\text{HP-FePO}_4}/B_{\text{berlinite}} = 4.8$, experimental $B_{\text{HP-FePO}_4}/B_{\text{berlinite}} = 4$; calculated $d_{\text{HP-FePO}_4}/d_{\text{berlinite}} = 1.35$, experimental $d_{\text{HP-FePO}_4}/d_{\text{berlinite}} = 1.27$), though the overestimation of volume within the GGA+U (see table 3) results in lower calculated densities than the experimental ones.

Figure 6 shows the calculated (PBE-GGA+U, $U = 4.5$ eV) enthalpy–pressure variation for the FePO₄ polymorphs (0 K). It can be observed that the berlinite form is

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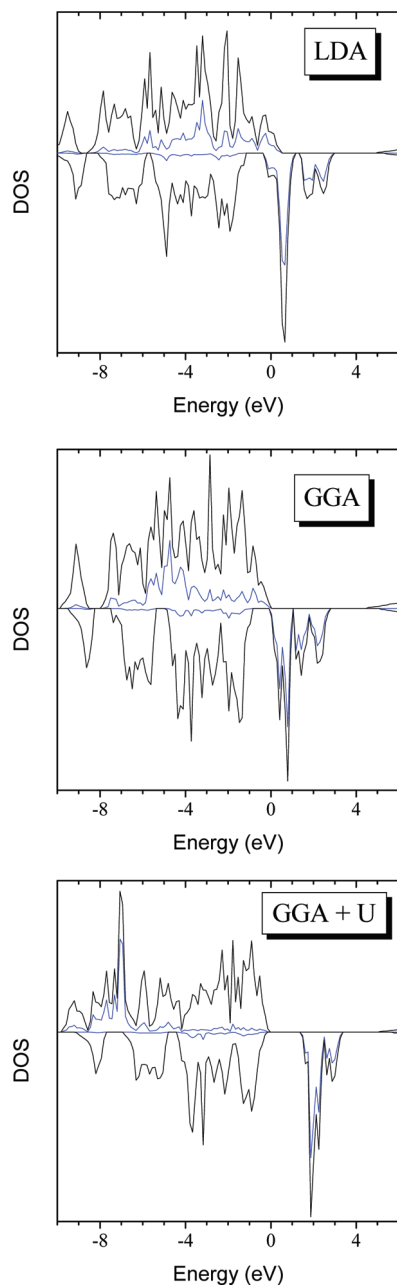


Figure 5. Calculated density of states (DOS) of HP-FePO₄ within the PP-LDA, PP-GGA and PBE-GGA+U ($U = 4.5$ eV) approximations. Black lines denote the total DOS, and the partial DOS of iron is represented in blue lines. The Fermi level has been arbitrarily chosen as the origin of the energy.

the most stable up to 2 GPa; above that pressure, the HP-FePO₄ polymorph is the thermodynamically stable phase. Heterosite and monoclinic forms remain metastable in the whole range of pressure. This is in a good agreement with the results of the high pressure synthesis performed in this work which proved that both berlinite and monoclinic phases convert into HP-FePO₄ for $P \geq 2$ GPa ($T = 900$ °C). There is also a good agreement with previous HP investigations in the FePO₄ system. We already reported that berlinite treated at 1.8 GPa at room

Table 4. Calculated Equation of State Parameters and Densities for FePO₄ Polymorphs (PBE-GGA+U, $U = 4.5$ eV); E_0 , V_0 , B_0 , and B'_0 Are the Zero-Pressure Energy, Volume, Bulk Modulus and Its Pressure Derivative, Respectively (All the Results Are Given Per Formula Unit); Experimental Data Are Given in Parentheses

polymorph	B_0 (GPa)	B'_0	V_0 (Å ³)	E_0 (eV)	rms ^b (meV)	density (g/cm ³)
berlinite	18.75 (24 ²⁹)	4.45	90.78	-42.798	0.18	2.76 (3.04 ^a)
monoclinic	26.22	2.20	87.72	-42.744	2.22	2.85 (3.05 ^a)
heterosite	58.37	2.81	71.76	-42.648	0.54	3.49 (3.67 ³⁴)
HP	90.14 (96 ²⁹)	4.32	67.08	-42.624	0.06	3.73 (3.89 ^a)

^a This work. ^b rms = $\sqrt{(\sum(E - E_{\text{fit}})^2/n)}$.

temperature does not transform to the HP form.¹¹ On the other hand, Pasternak et al. collected angle-dispersive XRD patterns obtained with increasing pressure and after decompression to ambient pressure (diamond anvil cells were utilized).²⁹ The diffraction peaks corresponding to the HP-FePO₄ phase first appear at $P = 2.5$ GPa, dominating the diffraction patterns at $P = 5$ GPa. They also determined that the stability range of the HP phase extends to at least 26 GPa. Interestingly, and to the best of our knowledge, no evidence of heterosite formation was detected in HP-experiments performed between ambient pressure and 30 GPa at various temperatures.^{10,11,29–31} As seen in Figure 6, the different FePO₄ polymorphs have close enthalpy values in the region 1.5–2 GPa, making synthesis approaches in this range of pressure very appealing to seek for novel FePO₄ polymorphs. Further work is in progress to perform in situ XRD studies in that pressure range and elevated temperature, which can very efficiently provide more insight into the pressure–temperature stability map of FePO₄ forms.

HP polymorphs are metastable phases at ambient pressure. However, due to kinetics barriers, they do not transform but stay in the HP structure even at ambient pressure. Increasing the temperature, at $p = 0$, enables metastable phases to transform to its thermodynamic stable form. Metastable heterosite and monoclinic varieties transform to berlinite at ca. 500 and 450 °C, respectively.⁶ This suffices to explain why these two metastable phases can be used in electrochemical Li cells at RT without any sign of transformation to the berlinite polymorph. The thermal stability of HP-FePO₄ has been first checked by DTA measurements. An exothermic event is observed (figure not shown) centred at about 710 °C. As expected, the powder diffraction pattern of the residue after the transition corresponds to the berlinite polymorph. This HP → berlinite transition is irreversible (the corresponding signal is not observed on cooling), suggesting that berlinite is the stable form of FePO₄, in good agreement with the GGA+U calculations. This phase transformation was also studied by collecting XRD patterns at different temperatures between RT and 800 °C. Figure 7 shows some relevant patterns on

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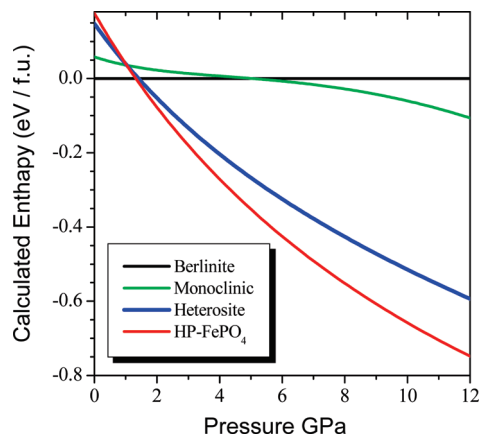


Figure 6. Calculated enthalpy vs pressure for FePO_4 polymorphs (PBE-GGA+U data with $U = 4.5$ eV).

heating and cooling, with the reflections corresponding to the berlinite phase indicated by arrows. The HP \rightarrow berlinite transition starts at a temperature of 600 °C and is completed at 700 °C. In the 600–700 °C range, both HP and berlinite coexist, suggesting that this is a first-order transition. In short, HP- FePO_4 irreversibly transforms upon heating to berlinite, as it occurs with the other known forms of FePO_4 (heterosite, monoclinic, and orthorhombic).

So far, the calculated stability map of Figure 6 is consistent with experimental results; (i) at ambient pressure, any FePO_4 polymorph converts irreversibly to the most stable berlinite phase; (ii) at pressure above 2 GPa, HP- FePO_4 is the thermodynamically stable polymorph. However, the high-temperature oxide melt solution calorimetry measurements reported by Iyer et al.¹³ opens an exciting point for discussion. These authors determined a positive enthalpy of 11.67 kJ/mol at 25 °C for the heterosite \rightarrow berlinite transition. In Figure 6, such transition has a calculated negative enthalpy of -0.027 eV/atom (-15.88 kJ/mol). One may argue that DFT results refer to 0 K; therefore, to match the experimental calorimetry results, the enthalpy of the transformation should vary from -15.88 kJ/mol at 0 K to 11.67 kJ/mol at 25 °C (enthalpy change of 27.55 kJ/mol). Utilizing additional computational data,³⁵ the estimated enthalpy of the heterosite- $\text{FePO}_4 \rightarrow$ berlinite- FePO_4 transformation at 25 °C is -14.4 kJ/mol (see the Supporting Information). Thus, there is a clear disagreement between high-temperature oxide melt solution calorimetry measurements and computational results. In addition, according to Iyer et al.,¹³ the berlinite \rightarrow heterosite transition on cooling is thermodynamically favored, but kinetically hindered. If this is the case, high-pressure/high-temperature experiments should help to induce the berlinite \rightarrow heterosite transition (densities are 3.04 and 3.67 g/cm³ for berlinite and heterosite, respectively). A legitimate question then arises: why does the berlinite form not transform under pressure into the denser heterosite form, which according to the calorimetry results is thermodynamically more stable?

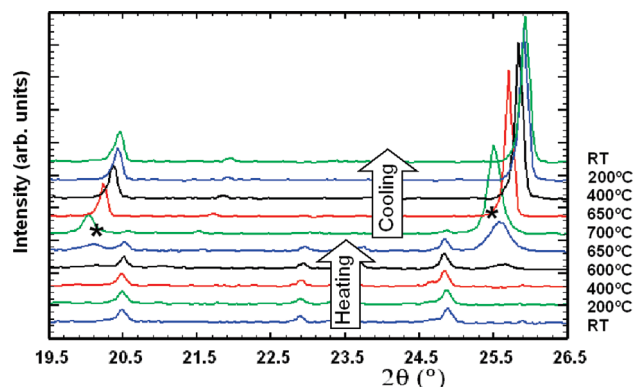


Figure 7. Powder XRD pattern of HP- FePO_4 at different temperatures showing the transition of HP- FePO_4 to the berlinite form (asterisks).

The above discrepancies might be originated by the nature of the heterosite sample utilized for the high-temperature oxide melt solution calorimetry experiments. This sample was prepared by chemical delithiation of LiFePO_4 using NO_2BF_4 in acetonitrile,^{13,32} a severe oxidizing agent. Although its XRD pattern corresponds to the heterosite form,³² it is questionable whether amorphous secondary phases or impurities could be present in the sample influencing the determination of the enthalpy of drop solution. The particles' morphology of the heterosite sample may also play a role. There are instances where high surface area or small particle size stabilize the high-temperature metastable phases at room temperature (see ref 33 and references therein). Thus, the tetragonal phase of ZrO_2 is stabilized at room temperature by small particle size; normally the tetragonal phase is formed around 1420 K. The possibility of particle's morphology affecting the thermodynamic stability of the FePO_4 polymorphs could also be taken into account.

Conclusions

The main goal of this work has been to investigate computationally and experimentally the energetic stability of known polymorphs of FePO_4 , in view of proposing synthesis routes conducting novel polymorphs with electrochemical activity in Li cells. We have proven that DFT computational methods utilizing GGA and LDA functionals (without introducing the Hubbard correction term, U) are not valid to investigate these polymorphs as they do not reproduce the physical properties of HP- FePO_4 . The DFT+ U method predicts that the berlinite (Fe^{3+} in tetrahedral environment, $d = 3.04$ g/cm³, $\rho_{\text{RT}} > 4 \times 10^{13}$ Ohm cm) is the most stable form up to 2 GPa. At higher pressures HP- FePO_4 (Fe^{3+} in octahedral environment, $d = 3.89$ g/cm³, $\rho_{\text{RT}} = 2.10^7$ Ohm cm) is the thermodynamically stable form. The intermediate

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density phases monoclinic-FePO₄ and heterosite are metastable at any pressure. We conclude that moderate pressure (below 2 GPa) synthesis methods (hydrothermal, solvothermal, or mechanical pressure as in the present work) could lead to novel FePO₄ polymorphs with enhanced electronic conductivity. Higher pressures (above 2 GPa) would produce excessively dense forms of FePO₄, with hindered lithium mobility, as is the case of HP-FePO₄.

The predicted relative stability of FePO₄ polymorphs within the DFT + U framework is consistent with the phase-transformations found for the various FePO₄ polymorphs under pressure and/or temperature, as shown by different techniques in this and previous works (in situ T-XRD, in-situ P-XRD, DSC, DTA). However, some discrepancies exist with reported high-temperature oxide melt solution calorimetry measurements, which found the

heterosite form to be energetically more stable than the berlinite form at 25 °C (ambient pressure). High-temperature oxide melt solution calorimetry measurements on HP-FePO₄ could help to resolve this controversy.

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Supporting Information Available: Additional calculations and figures on heat capacity (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.