

Is it possible to prepare olivine-type LiFeSiO_4 ? A joint computational and experimental investigation

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Abstract

Silicates LiMSiO_4 are potential positive electrode materials for lithium ion batteries. In this work we analyse from first principles calculations the relative stability of possible LiFeSiO_4 -polymorphs within four structural types. Olivine- LiFeSiO_4 is predicted to be more stable than the LiFeSiO_4 prepared by delithiation of $\text{Li}_2\text{FeSiO}_4$; the latter being the only LiFeSiO_4 compound reported so far. Attempts to prepare olivine- LiFeSiO_4 from a mixture of reactants at ambient pressure (600–1100 °C) resulted in a mixture of quartz- SiO_2 , Li_2SiO_3 , LiFe_5O_8 and $\text{LiFeSi}_2\text{O}_6$ phases. Conducting the reaction under HP conditions (40 kbar) leads to the formation of $\text{LiFeSi}_2\text{O}_6$ as a majority phase, regardless the nature of the reactants/precursors. First principles calculations indicate that the preparation of the olivine- LiFeSiO_4 is thermodynamically hindered due to the competition with the more stable $\text{LiFeSi}_2\text{O}_6$ pyroxene, in the range of pressure/temperature investigated.

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1. Introduction

Current trends focus on silicates as the next generation of lithium-ion battery electrode materials. The use of Li_2MSiO_4 as cathode materials was suggested as early as 1997 [1] and the electrochemistry of $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$ towards Li^+/Li has been reported since, showing that these compounds are electrochemically active at average voltages of *c.a.* 3.1 V and 4.2 V, respectively [2,3]. Regarding possible LiMSiO_4 silicates, LiFeSiO_4 is only known to exist as derived from $\text{Li}_2\text{FeSiO}_4$ by lithium deinsertion [2], while the existence of any LiMnSiO_4 compound has not been reported so far. However, olivine LiMSiO_4 compounds have been investigated from first principles; the predicted deintercalation voltage of olivine- LiMSiO_4 being

4.97 V and 4.87 V for $M=\text{Fe}$ and Mn , respectively [4]. In the case of LiFeSiO_4 the calculated volume expansion is of only 1%.

Aiming to prepare novel silicates of formula LiFeSiO_4 in the first part of this work we have performed a computational investigation on the relative stability of possible LiFeSiO_4 polymorphs, within four candidate structural types: delithiated- $\text{Li}_2\text{FeSiO}_4$, olivine, Na_2CrO_4 -like and spinel. The choice of these structures is based on previous studies on olivine LiFeXO_4 compounds ($X=\text{P}$, As), where the spinel and the Na_2CrO_4 structures were detected as stable forms [5,6]. While the $\text{Li}_2\text{FeSiO}_4$ structure presents a quasi-2D skeleton where each SiO_4 tetrahedron shares its four corners with four neighbouring FeO_4 tetrahedra, the remaining candidate structures are three-dimensional frameworks with Fe ions in octahedral coordination (see Fig. 1). In a second part of this work, first principle calculations have been used to guide the selection of the experimental conditions (pressure/temperature) that could lead to the preparation of olivine- LiFeSiO_4 .

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2. Methodology

2.1. Computational

The total energy of LiFeSiO₄ in within the Li₂FeSiO₄, olivine, Na₂CrO₄ and spinel structures were calculated using the Projector Augmented Wave (PAW) method as implemented in the Vienna *Ab-initio* Simulation Package (VASP) [7]. The exchange and correlation energies have been approximated in the Generalized Gradient Approximation with the Hubbard parameter correction (GGA+*U*) [8] with values of *U*=6 eV and *J*=1 eV for Fe atoms. The same methodology was used to calculate the total energies of Fe₂O₃, Li₂SiO₃, SiO₂, and LiFeSi₂O₆. The structure of delithiated-LiFeSiO₄ was taken from a previous computational study [9]. As a first step the LiFeSiO₄ structures were fully relaxed (cell parameters, volume and atomic positions); the final energies of the optimized geometries were recalculated so as to correct for the changes in the basis set of the wave functions during relaxation. Secondly, relaxed structure calculations were performed at various constant volumes and the energy–volume data was fitted to the Murnaghan equation of state [10]

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

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. Other computational and structural details can be found in references [4,9,11,12].

2.2. Experimental

Synthesis of LiFeSiO₄ was attempted by solid state reaction starting from a mixture of Fe₂O₃ (obtained from the thermal decomposition of Fe(NO₃)₃ · 9 H₂O), Li₂SiO₃ (Alfa-Aesar 99.5%) and SiO₂ (Aldrich 99.9% fused granulated) in stoichiometric amounts that was milled at 15 s⁻¹ for 10 min. Different portions of the mixture were treated, pelletized, at temperatures ranging from 600 to 1100 °C at room pressure. Experiments at 40 kbar were performed using the same mixture of reactants, at temperatures of 600 °C and 900 °C. The high-pressure experiments were performed on a belt-type press working at a maximum pressure of 8 GPa and 1200 °C. X-ray powder diffraction patterns (XRDP) were collected on a Philips X'Pert diffractometer using a monochromatic Cu Kα1 radiation (λ=1.54056 Å), between 5–75° (2θ) with a step width 0.02° (2θ) and a counting time of 6 s.

3. Results and discussion

Fig. 2a shows the relative energy vs. the equilibrium volume of LiFeSiO₄ compounds within the chosen structural types, together with the corresponding fit of the DFT data to the Murnaghan equation of state [10]. A remarkable volume decrease is observed when going from the delithiated-LiFeSiO₄ structure (2D character with Fe in tetrahedral sites) to

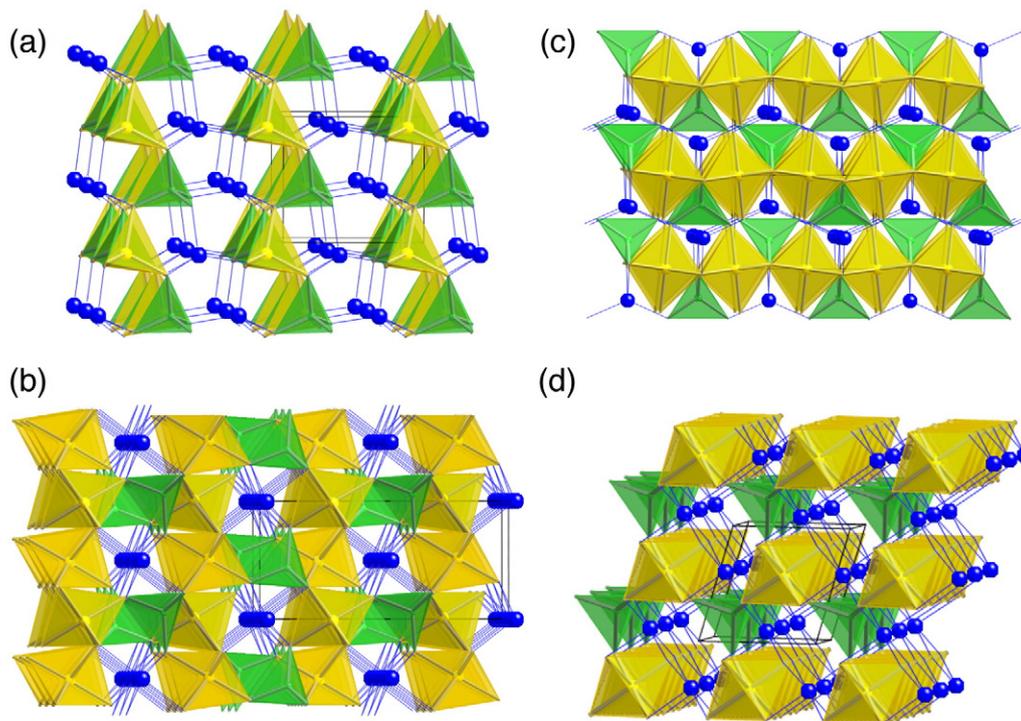


Fig. 1. The optimized structures of (a) delithiated-LiFeSiO₄, (b) olivine-LiFeSiO₄, (c) Na₂CrO₄-like LiFeSiO₄ and (d) spinel-LiFeSiO₄. Lithium ions are indicated by blue balls, and green and yellow polyhedra denote Si and Fe, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

any other polymorph (3D-character with Fe in octahedral sites). According to the calculated data, LiFeSiO_4 is less stable in the delithiated- $\text{Li}_2\text{FeSiO}_4$ structure than in the denser olivine or Na_2CrO_4 forms. This is to say, delithiated- LiFeSiO_4 is predicted to be a metastable compound. Soft chemistry routes, as electrochemical lithium deinsertion, have long been used to produce metastable compounds that are not accessible by high-temperature solid state reactions. Hence, it is not surprising that delithiation of $\text{Li}_2\text{FeSiO}_4$ would result in a metastable LiFeSiO_4 compound. Among the studied LiFeSiO_4 polymorphs, the olivine phase is predicted to be the most stable one, with a volume contraction of about 15% with respect to delithiated- Li_2MSiO_4 . Fig. 2b shows the calculated enthalpy-pressure variation for the LiFeSiO_4 polymorphs. It can be observed that the olivine polymorph is effectively predicted as the thermodynamically stable phase below 140 kbar. At higher pressures the stable form is the spinel structure.

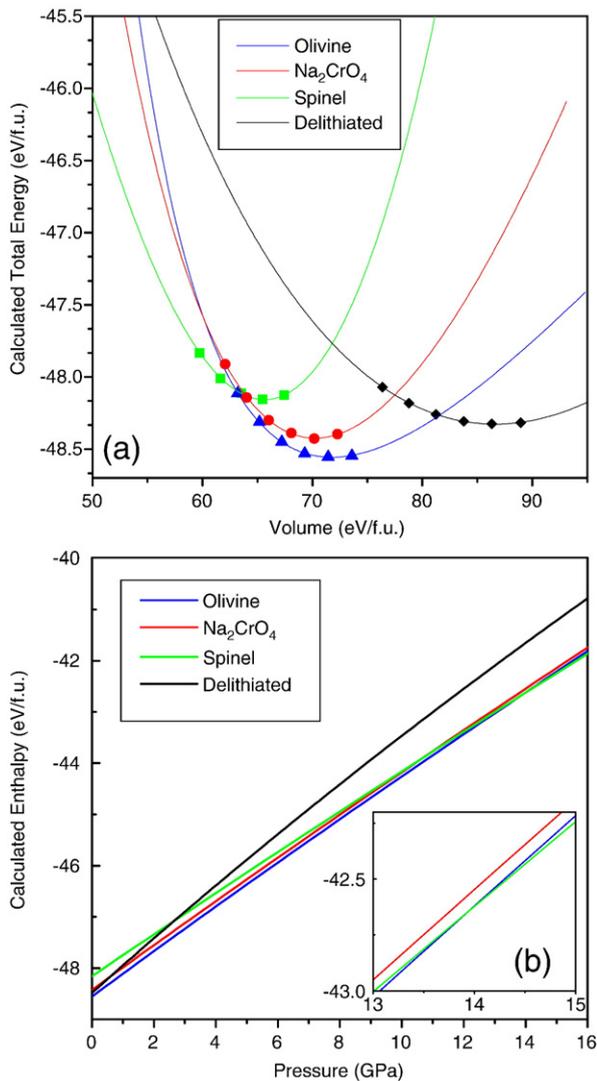


Fig. 2. (a) Calculated total energy difference between possible LiFeSiO_4 polymorphs in the delithiated- $\text{Li}_2\text{FeSiO}_4$, olivine, Na_2CrO_4 and spinel structures vs. the equilibrium volume. (b) Relative stability of possible LiFeSiO_4 as a function of pressure. The inset enlarges the region between 13 and 15 GPa.

Table 1

Calculated cell volume for the optimized structures of the compounds involved in this investigation

Compound	Volume ($\text{\AA}^3/\text{f.u.}$)
LiFeSiO_4	86.31
Spinel- LiFeSiO_4	65.47
Na_2CrO_4 like- LiFeSiO_4	70.16
Olivine- LiFeSiO_4	71.43
Quartz- SiO_2	39.22 (37.67 [13])
Li_2SiO_3	60.6 (59.08 [14])
$\alpha\text{-Fe}_2\text{O}_3$	51.89 (50.39 [15])
$\text{LiFeSi}_2\text{O}_6$	107.20 (104.15[16])

Experimental volumes are given in parentheses.

Thus, the question is whether it is possible to synthesize the predicted most stable polymorph; olivine- LiMSiO_4 . In the simplest case, olivine- LiMSiO_4 compound could be prepared from a mixture of reactants according to the reaction:

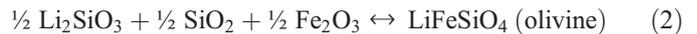


Table 1 lists the calculated cell volume of all the compounds involved in reaction (2) confronted to the experimental ones. As can be seen, there is a good agreement between experimental and calculated volume, with the calculated parameters being slightly overestimated with respect to the experimental ones, as usually found within the GGA approximation. Calculated volume of hypothetical olivine, spinel and Na_2CrO_4 -like LiFeSiO_4 are expected to be overestimated as well. From the calculated total energies of Li_2SiO_3 , SiO_2 , Fe_2O_3 and LiFeSiO_4 we can infer the energy of reaction (2), according to the expression:

$$\begin{aligned} \text{Reaction energy} = & E_{\text{total}}(\text{LiFeSiO}_4) - 1/2 E_{\text{total}}(\text{Fe}_2\text{O}_3) \\ & - 1/2 E_{\text{total}}(\text{SiO}_2) \\ & - 1/2 E_{\text{total}}(\text{Li}_2\text{SiO}_3) \end{aligned} \quad (3)$$

The calculated energy is positive, with a value of 0.11 eV. The reaction is accompanied by a volume contraction, $\Delta V = \sum V_{\text{reactants}} - V_{\text{product}}$, of $\Delta V = -4.425 \text{ \AA}^3$. These results suggest that the endothermic reaction (2) could be favoured under high-pressure conditions. In a rough approximation, at 0 K, the estimated pressure required to induce reaction (2) is of the order of 40 kbar ($P \approx -\Delta E/\Delta V$). However, high-pressure synthesis should be performed at high temperature to allow ionic diffusion. In reaction (2), the entropy content of the reactants is expected to be larger than that of the products ($\Delta S_{\text{reaction}} < 0$), and at elevated temperatures the entropy term will contribute to increase the free energy of reaction (2), in opposition to the effect of pressure. The appropriate combination of pressure and temperature to obtain olivine- LiMSiO_4 should be determined experimentally.

Firstly we attempted reaction (2) at ambient pressure. Selected XRPD of the products are shown in Fig. 3. At 600 °C LiFe_5O_8 is detectable in the XRPD, together with substantial amounts of Fe_2O_3 and Li_2SiO_3 . At 800 °C a small amount of $\text{LiFeSi}_2\text{O}_6$ appears together with LiFe_5O_8 as reaction products.

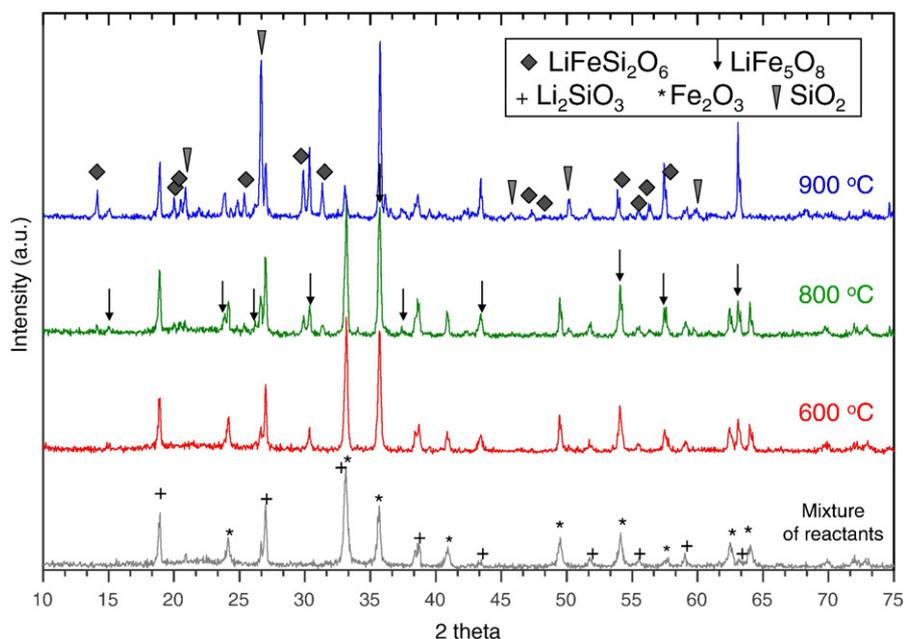
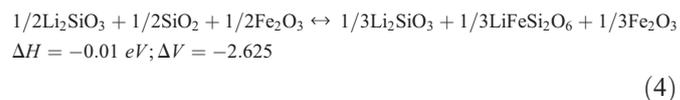


Fig. 3. Selected XRD patterns of the products of reaction (2) obtained at ambient pressure and temperatures from 600 °C to 1000 °C.

A temperature above 800 °C is necessary to fully react Fe_2O_3 . At 900 °C quartz- SiO_2 crystallizes, and a mixture of quartz- SiO_2 , Li_2SiO_3 , LiFe_5O_8 and $\text{LiFeSi}_2\text{O}_6$ phases is detectable in the XRDP. The reaction mixture melts at about 1000 °C.

Attempts to produce reaction (2) performed at 40 kbar resulted in red-brownish and dark-grey powders at 600 °C and 900 °C, respectively. The corresponding XRDP are shown in Fig. 4. At 600 °C while most of the Fe_2O_3 and Li_2SiO_3 remain unreactive, the formation of $\text{LiFeSi}_2\text{O}_6$ already occurs. In comparison with Fig. 3, at the same temperature of 600 °C,

pressure enhances the formation of $\text{Li}_2\text{FeSi}_2\text{O}_6$. According to the formation of these products, the HP driven reaction could be written as:



Reaction (4) has a negative ΔV , explaining why $\text{LiFeSi}_2\text{O}_6$ appears as a majority phase at 40 kbar, but not at ambient pressure conditions (compare Fig. 3 with Fig. 4). Increasing the

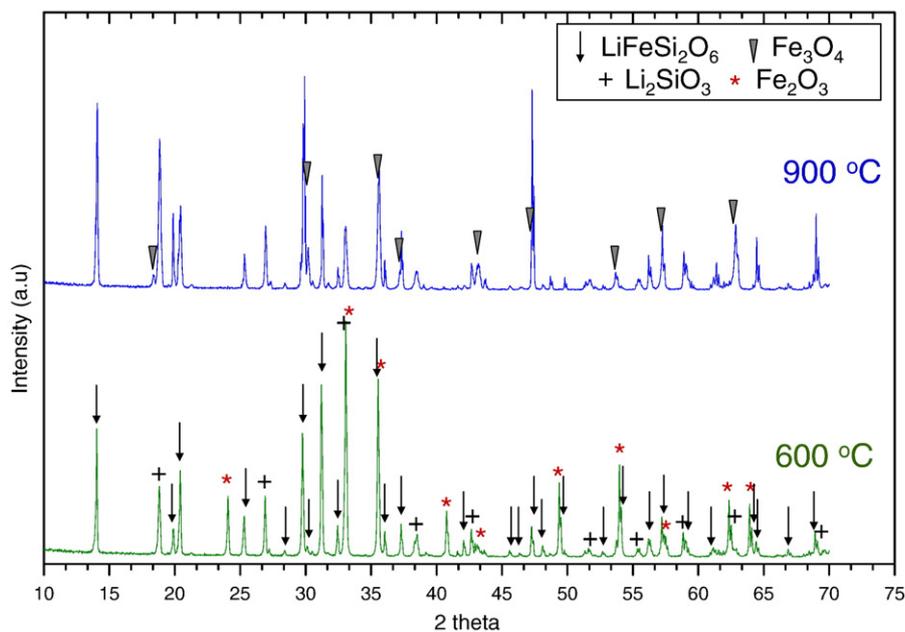
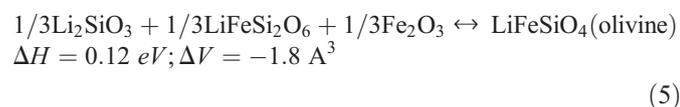


Fig. 4. XRD patterns of the products of reaction (2) obtained at a pressure of 40 kbar.

temperature up to 900 °C at the same pressure (40 kbar) completes the reaction of Fe₂O₃ in favour of a larger amount of LiFeSi₂O₆, together with some Fe₃O₄ and Li₂SiO₃.

We did also attempt reaction (2) starting from different reactants, and a precursor obtained in acid media, to avoid the formation of Li₂SiO₃ (details are not provided for conciseness). Even though the amount of Li₂SiO₃ is substantially decreased, LiFeSi₂O₆ still appears as the majority phase. This confirms that the formation of LiFeSi₂O₆ does not depend on the nature of the reactants.

The formation of the LiFeSi₂O₆ (reaction (4)) prevents the obtention of LiFeSiO₄ (reaction (2)). This is to say, that reaction (4) competes with reaction (2). The exothermic reaction (4) is clearly thermodynamically favoured vs. the endothermic reaction (2). Thus, the question is now if olivine-LiFeSiO₄ could be prepared according to the reactions (2)–(4):



In a rough approximation, the order of the pressure required for reaction (5) is of about 107 kbar. As shown in Fig. 2b, the olivine form is the most stable among the investigated polymorphs up to 140 kbar. Hence, high-pressure experiments in the range 107–140 kbar might overcome the formation of the LiFeSi₂O₆ piroxene in favour of olivine-LiFeSiO₄. Further work is in progress to perform in situ studies at those high-pressures/high-temperature conditions, which can provide much more insight into the possibility of preparing olivine-LiFeSiO₄.

4. Conclusions

Delithiation of Li₂FeSiO₄ (Fe²⁺ in tetrahedral sites) leads topotactically to LiFeSiO₄. In the present work, total energy calculations indicate that there is a driving force for LiFeSiO₄ to crystallize in denser structures based on octahedrally coordinated Fe⁺³ ions. Among the candidate structures studied, the olivine-like form presents the minimum of energy. Attempts to prepare olivine-LiFeSiO₄ from a mixture of reactants at ambient

pressure were unsuccessful, and resulted in a mixture of quartz-SiO₂, Li₂SiO₃, LiFe₅O₈ and LiFeSi₂O₆ phases. Conducting the reaction under HP conditions (40 kbar) enhances the reactivity of the mixture of reactants, but leads to the formation of LiFeSi₂O₆ as a majority phase. First principles investigations indicate that the obtention of the olivine-LiFeSiO₄ is thermodynamically precluded due to the competition with the more stable pyroxene-LiFeSi₂O₆ (Fe³⁺ in octahedral sites) in the range of pressure/temperature utilized in this investigation.

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