Theoretical study of the scheelite-to-fergusonite phase transition in YLiF$_4$ under pressure

J. López-Solano[a,*], P. Rodríguez-Hernández[a], A. Muñoz[a], F.J. Manjón[b]

[a]Dpto. de Física Fundamental II, Universidad de La Laguna, La Laguna, Tenerife, Spain
[b]Dpto. de Física Aplicada, Universitat Politècnica de València, València, Spain

Abstract

Recent experimental works on high-pressure X-ray diffraction have shown that YLiF$_4$ undergoes a reversible phase transition around 10 GPa from the ambient pressure scheelite-type to a fergusonite-type structure. Different theoretical works have proposed either the M-fergusonite or M′-fergusonite as this second stable structure. Also, small changes in photoluminescence and Raman signals have been observed around 6 GPa, and have not been completely explained yet. In this work we present a first-principles Density Functional Theory structural study of YLiF$_4$. We found that the anomalies at 6 GPa can be related to the structural changes observed in a scheelite to M′-fergusonite transition. We also have studied briefly different possibilities for an experimentally observed but not completely characterised third stable structure above 17 GPa.
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1. General remarks

YLiF$_4$ is an ambient pressure tetragonal scheelite compound, commonly used as a laser host material for trivalent rare-earth ions in industry. This laser material has received considerable attention in the last years and several experimental and theoretical studies under pressure have been published [1–9]. Recent experimental works show YLiF$_4$ undergoes a reversible phase transition around 10 GPa [1,3–5]. In particular, XRD measurements have shown that this transition is from the tetragonal scheelite to a monoclinic M-fergusonite structure, and that there is another phase transition around 17 GPa to an unresolved structure [5].

On the theoretical side, Molecular Dynamics methods propose a first phase transition from scheelite to a M′-fergusonite at a low pressure of 6 GPa, and a second phase transition to another structure also with the same symmetry as the M′-fergusonite [6]. The most recent calculations on YLiF$_4$ using ab initio Density Functional Theory, agree on the experimental results for the first phase

transition, and claim the third structure (second high-pressure phase) is wolframite [7].

Finally, recent photoluminescence (PL) measurements of Er^{3+}, Nd^{3+} and Pr^{3+} ions under pressure in this laser material show some anomalies around 5–7 GPa [1,3,4]. These anomalies seem to bear no clear correlation with the experimentally observed structural features [5]. The authors attributed these anomalies to some possible subtle structural instabilities of the scheelite structure. In particular, a possible transformation between two different scheelite polytypes with different setting angles has been recently proposed [8] based on the assumption that the LiF$_4$ tetrahedra remain undistorted but rotate under pressure, as suggested by Sen et al. [9]. In this work, we perform a theoretical study of YLiF$_4$ in the framework of the Density Functional Theory, trying to give a different explanation to these anomalies, analysing various structures proposed as stable in previous experimental and theoretical works.

2. Theoretical calculation details

As candidates to be stable in the low pressure range, we studied the scheelite (SG: I4$_1$/a, no. 88, Z = 4),

*Corresponding author. Tel.: +34 922318275; fax: +34 922318320.
E-mail address: javierl@marengo.dfis.ull.es (J. López-Solano).

M-fergusonite (SG: C2/c, no. 15, $Z = 4$), and M′-fergusonite (SG: P2$_1$/c, no. 14, $Z = 4$) structures. Note that we carried out all the calculations of M-fergusonite in the C12/c1 standard setting and then translated the structural parameters to the I12/a1 setting, to allow an easier comparison with the scheelite and M′-fergusonite structures. For the high-pressure range, we studied both structures found stable in previous theoretical works, namely the wolframite (SG: P2/c, no. 13, $Z = 2$) and the structure proposed in Ref. [6] (SG: P2$_1$/c, no. 14, $Z = 4$), and also the LaTaO$_4$-type (SG: P2$_1$/c, no. 14, $Z = 4$), BaWO4-II (SG: P2$_1$/c, no. 14, $Z = 8$), pseudoscheelite (SG: Pnma, no. 62, $Z = 4$), and baddeleyite (SG: P2$_1$/c, no. 14, $Z = 2$) structures.

All our ab initio calculations were performed with the VASP code [10], using the Projector Augmented Waves (PAW) [11] pseudopotentials supplied with the package [12], within the Generalised Gradient Approximation (GGA) [13] for the exchange and correlation energy. The improved tetrahedron method with Blöch corrections [14] was used for the Brillouin-zone integrations.

In order to achieve high precision results, we raised the plane-waves energy cut-off to 1300 eV, and the cut-off for the augmentation charges to 1500 eV. Together with fine k-point grids, using the usual Monkhorst–Pack scheme, this assures a convergence of 2 meV per formula unit for the total energy of each structure considered, and 0.1 GPa for its pressure. It should also be noted these settings guarantee a good comparison between the smallest, 12 atoms per primitive cell structures, and the biggest ones. We performed some calculations, at the same volume per formula unit, of the M-fergusonite structure represented as a C2/c 12-atoms primitive cell, and as a P2$_1$/c 24-atoms supercell, and found energy differences of less than 1 meV per formula unit. For each structure studied, full relaxation of the internal and cell parameters was performed to achieve forces over the atoms below 0.006 eV/Å, and differences between the diagonal components of the stress tensor below 0.1 GPa. The energy-volume data pairs obtained were then fitted to a Birch–Murnaghan 4th-order equation of state (EOS) [15] to obtain the pressure and the values of the bulk modulus and its first derivative with respect to the pressure at zero pressure. As a further indication of the quality of the calculations performed, the pressures given by these EOS fits agreed with the ones reported by VASP. With all this information, we calculated the enthalpy to determine the stable phase at each pressure.

3. Results

At low pressures, we found that both M- and M′-fergusonites, have the same energy as the scheelite structure (see Fig. 1). Structurally, both fergusonites have an a and c (b) lattice parameter equal to the a (c) one of the scheelite (Fig. 2), and a monoclinic beta angle near 90° (Fig. 3). Both fergusonites are thus reduced to scheelite, which we found
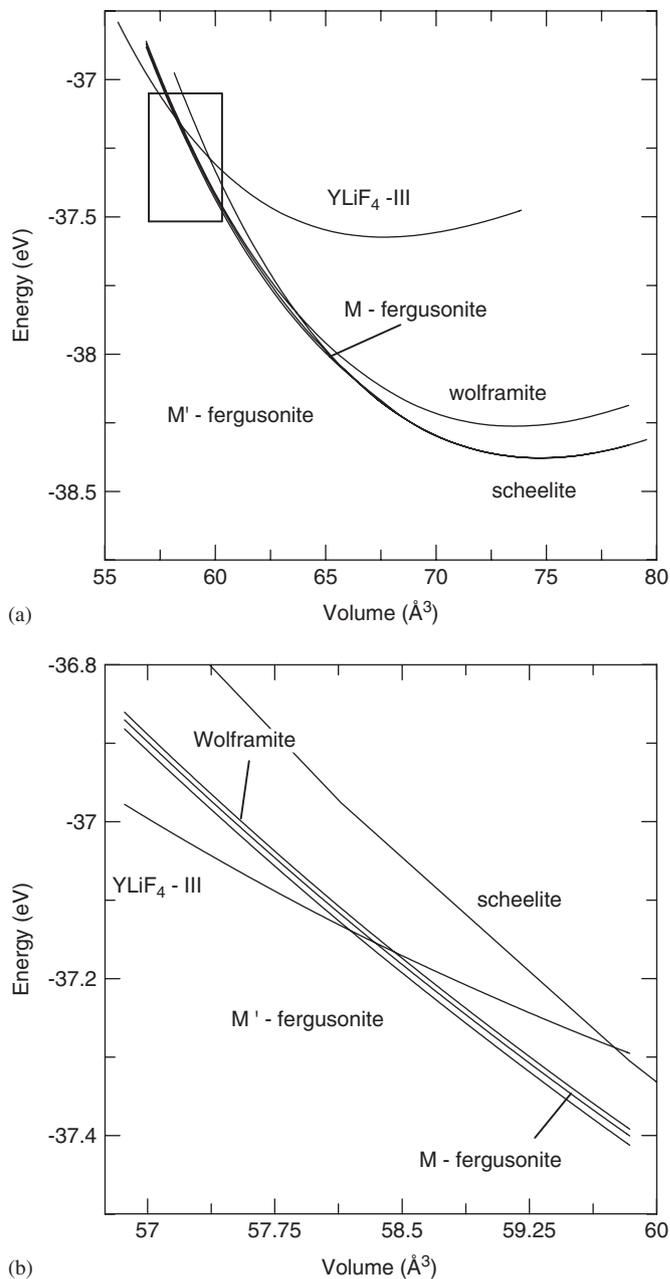
Fig. 1. (a) Energy–volume curves for some of the structures considered in this work (see text). All extensive magnitudes are written per formula unit; (b) Extended region of the second high-pressure phase transition marked in (a). The structure labelled as YLiF4-III is the high-pressure one found by Sen et al. [6].

as the stable ambient pressure phase, in agreement with experimental reports.

Table 1 summarizes the equilibrium volume per formula unit (pfu), the bulk modulus and its first derivative for the scheelite structure compared to the values from previous experimental and theoretical results. We also include our results obtained with PAW pseudopotentials within the Local Density Approximation (LDA) for the exchange-correlation energy. As can be seen, our results with GGA, despite overestimating the equilibrium volume (as usual with this approximation) are closer to the experimental
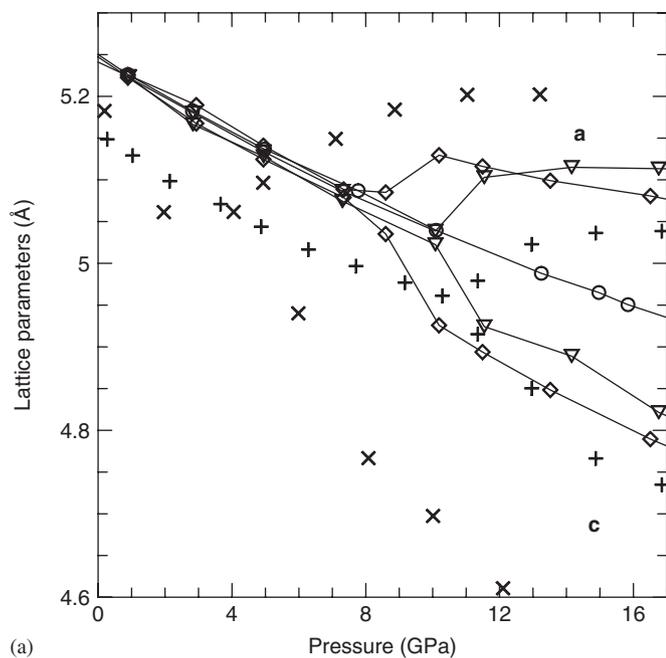
(a)
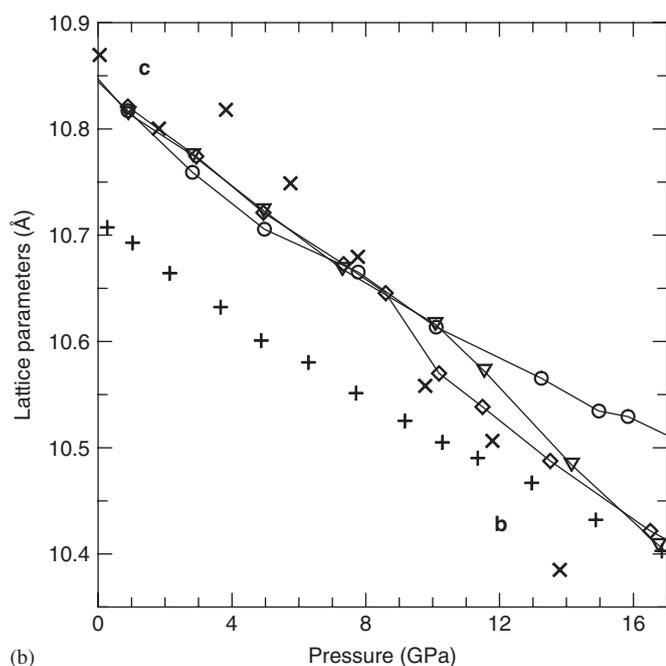
(b)

Fig. 2. Pressure dependence of the lattice parameters of the scheelite (circles), the M-fergusonite (triangles), and M′-fergusonite (diamonds). (a) scheelite a parameter and M- and M′-fergusonite a and c parameters; (b) scheelite c parameter and M- and M′-fergusonite b parameter. Experimental results after Ref. [5] (plus signs) and theoretical results after ref. [6] (crosses) are also shown for comparison.
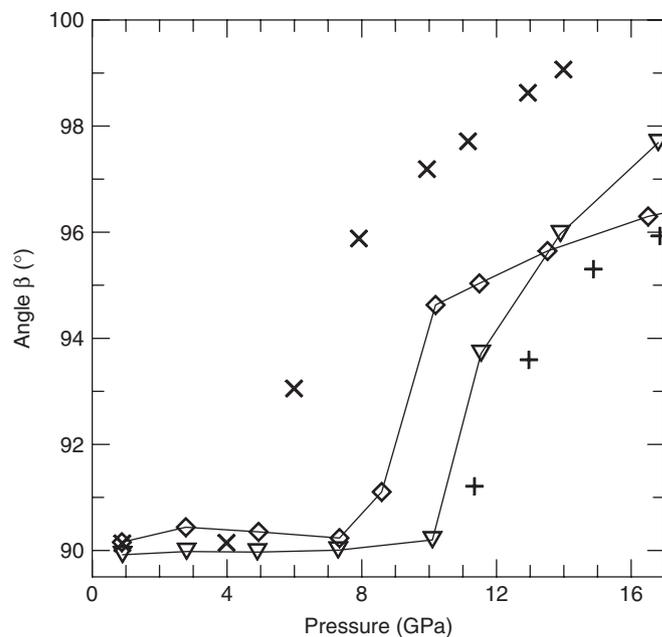
Fig. 3. Pressure dependence of the monoclinic beta angle for the M-fergusonite (triangles) and M′-fergusonite (diamonds). Experimental results after Ref. [5] (plus signs) and theoretical results after Ref. [6] (crosses) are also shown for comparison. Note that in Ref. [5] the scheelite structure, which corresponds to a beta angle of 90°, was observed till 10.6 GPa.

values than the LDA ones (which specially gives a much worse bulk modulus than GGA). Our results agree reasonably with those found in other theoretical works [6,7], while our values of the bulk modulus and its first derivative are somewhat closer to the experimental ones that those from Ref. [7] (in which the B_0' value was fixed at 4.97).

Upon increasing pressure, at 7.5 GPa the M′-fergusonite cell and internal parameters start to differentiate from the scheelite ones. This is in good agreement with the calculations from Sen et al. which show the transition from scheelite to M′-fergusonite at 6 GPa. However, until 11.6 GPa we do not observe an enthalpy difference between both phases (see Fig. 4), so in our calculations both coexists in a 4 GPa pressure range. The low volume change in this transition, as can be seen in Fig. 5, together with the previous results for the energy and structural parameters, classifies it as a second order transition, in agreement with the experimental observations. Results for V_0, B_0 and B_0' are presented in Table 2.

Table 1

Equilibrium volume per formula unit, bulk modulus and its first derivative, of the scheelite phase

	Ref. [5] Expt.	Ref. [6] Th. MD	Ref. [7] Th. US-LDA	Ref. [7] Th. PAW-GGA	This work PAW-LDA	This work PAW-GGA
$V_0(\text{Å}^3)$	143.22	148.75	136.37	146.93	136.83	149.50
$B_0(\text{GPa})$	81.0	—	122.2	94.8	95.0	77.3
B_0'	4.97	—	4.97	4.97	4.59	4.52

We quote experimental results from Ref. [5] and also other theoretical results from Refs. [6,7].
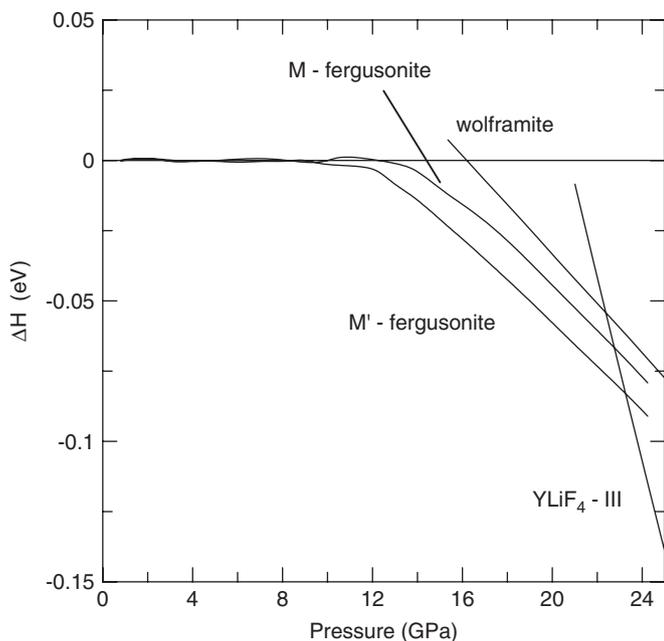
Fig. 4. Variation of enthalpy (per formula unit) with pressure. The enthalpy of the scheelite phase has been taken as reference. The post fergusonite stable structure proposed by Sen et al. is marked as YLiF$_4$-III.

Fig. 5. Volume (per formula unit) versus pressure for the I4$_1$/a scheelite (circles) and P2$_1$/c M'-fergusonite (diamonds) structures. Experimental results after Ref. [5] (plus signs) and theoretical results after Ref. [6] (crosses) are also shown for comparison.

The value of 11.6 GPa for the pressure of the first phase transition is in good agreement with the 10 GPa value obtained experimentally by Grzechnick et al. and also with the 9.3 GPa value obtained theoretically by Li et al. (but it should be noted that the later work did not consider the

Table 2
Equilibrium volume, bulk modulus and its first derivative for the second stable phase found in different works

	Ref. [5] Expt. M-fergusonite	Ref. [7] Th. PAW-GGA M-fergusonite	This work PAW-GGA M'-fergusonite
V_0 (Å^3)	143.22	146.32	149.50
B_0 (GPa)	81.0	95.3	79.1
B'_0	4.97	4.97	4.28

We include the same results from Grzechnick et al. shown in Table 1, since they were calculated from data of M-fergusonite and scheelite (or M-fergusonite reduced to scheelite). Note that Sen et al. also found the M'-fergusonite to be the second stable structure, though they did not give data to include in this table.

M'-fergusonite structure). Although we predict a transition to M'-fergusonite, the structural and energy differences with the M-fergusonite are rather small at these pressures. According to our calculations, the M-fergusonite phase suffers the departure from the scheelite structurally at 10 GPa and in enthalpy at 13 GPa, and from there on remains about 20 meV pfu in energy above the M'-fergusonite. Such a small energy difference (which is however well above our precision of 1–2 meV pfu) could perhaps disappear taking into account temperature effects (as indicated in Ref. [6]). However, the experimentally observed anomalies of the scheelite phase can be better explained in base to a scheelite to M'-fergusonite phase transition such as the one described in this work.

Fig. 6a shows the Raman shifts measured in YLiF$_4$ as a function of pressure in Refs. [2,4]. A clear change of pressure coefficient and the appearance of several modes is observed between 5 and 7 GPa. Fig. 6b shows the pressure dependence of the frequencies of a PL line of Eu^{3+} in YLiF$_4$ and of Nd^{3+} in YLiF$_4$ as obtained from Refs. [1,3], respectively. Again, changes are observed at 5–7 GPa. All these experimental features observed in the scheelite phase on increasing pressure can be related to the slow, second order transition from scheelite to M'-fergusonite which starts at 7.5 GPa but is not complete until 11.6 GPa, with the cell changes shown in Figs. 2 and 3, and the interatomic distances behaviour shown in Fig. 7.

In ref. [8], the anomalies were explained by a polytype transformation between two scheelite structures. This interpretation was based on ion rigid calculations [9], which claim that the responsible for the negative Grüneissen parameter of the lowest transversal E_g mode, related to the vibration of adjacent LiF$_4$–LiF$_4$ tetrahedra in the x–y plane perpendicular to the tetragonal axis [16], is the rotation of the LiF$_4$ tetrahedra along the c axis of the scheelite. However, it could be related also to the change of one of the second near-neighbour Li–F distance with increasing pressure produced by the different change of the scheelite lattice parameter a in the x and y directions to give the a and c lattice parameters of the M'-fergusonite structure. This change of the second Li–F neighbour is

(a)

(b)

Fig. 6. (a) Pressure dependence of the Raman shifts in $YLiF_4$ at 300 K, after Refs. [2,4]; (b) Pressure dependence of the PL wavenumber of the $^7F_4$ level of Eu^{3+} at 300 K (after Ref. [1]), and of the $^4I_{9/2}$ level of Nd^{3+} at 5 K (after Ref. [3]). Changes of the Raman and photoluminiscence frequencies between 5 and 7 GPa are evident in the figures.

Fig. 7. Evolution with the pressure of the interatomic distances below 3 Å between Li and F (upper pannel), and Y and F (lower pannel) neighbours in the scheelite structure (circles), the M-fergusonite (triangles), and the M′-fergusonite (diamonds). Experimental results after Ref. [5] (plus signs) are also shown for comparison.

present in the scheelite to M′-fergusonite transition, as can be seen in Fig. 7. Besides, this figure shows a stiffening of the first neighbour Li–F distance, starting at 7.5 GPa and very noticeable at 10 GPa, that matches with experimental observation [5]. The marked decrease of the first neighbour Li-F distance in the scheelite phase and the stiffening of this Li–F distance above 7.5 GPa allow to explain the extremely high positive Grüneissen parameter of the topmost E_g mode of the scheelite structure and its decrease above 7 GPa [2].

We will now talk briefly about the second phase transition of $YLiF_4$. Experimentally, Grzechnick et al. observed a new structure above 17 GPa, but they could not fully characterise it [5]. Calculations by Li et al. suggest that this high-pressure phase is a wolframite structure, stable from 17.6 GPa, whereas Sen et al. give a 16 GPa transition pressure to a structure of the $P2_1/c$ space group. In our calculations, the wolframite structure remains 20–30 meV pfu above the M′-fergusonite, which we find stable up to 23.3 GPa, when a second $P2_1/c$ structure (marked as $YLiF_4$-III in Fig. 4), structurally in agreement with the one proposed by Sen et al., clearly becomes the lowest enthalpy phase. Note that Li et al. did not consider this structure. As for the other structures studied in this work, namely the $LaTaO_4$, $BaWO_4$-II, pseudoscheelite and baddeleyite, none was found stable in the pressure range studied in this work.

The difference between our calculated transition pressure value of 23.3 GPa and the experimental value of 17 GPa may be due to the lack of temperature effects in our calculations and/or the use of the GGA for the exchange-correlation, which could be greatly overestimating the pressure. However, since our pressure for the first phase transition agrees quite nicely with the experimental value, it is also possible that other structure, not considered in this work, could be stable at a lower pressure.

4. Summary and conclusions

In this work we have reported an ab initio theoretical study of the pressure evolution of the $YLiF_4$ compound. At ambient pressure, our results for the scheelite structure agree with previous experimental and theoretical works. Upon increasing pressure, our results agree with recent Molecular Dynamics calculations in predicting a transition to the M′-fergusonite structure, instead to the M-fergusonite as in Refs. [5,7]. However, it must be noted that both M- and M′-fergusonites are very similar structural and energetically. The behaviour of the lattice parameters and Li–F interatomic distances in the scheelite-to-M′-fergusonite transition in the range of pressures of 7.5–10 GPa, as calculated in this work, may explain the anomalies in the Raman and PL spectra observed experimentally. As for the second phase transition, our results again agree qualitatively with the MD calculations, predicting a transition to another $P2_1/c$ structure. However, the difference between our calculated transition pressure and the experimental one leaves open the possibility of another structure being stable at high pressures, instead of the one found in this work. Further experimental work on $YLiF_4$ in the high-pressure range may be needed to completely characterize this third structure.

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