# Theoretical study of the $YLiF_4$ phase transitions under pressure

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Experimental work has shown that $YLiF_4$ has a first phase transition from the ambient pressure scheelite to a fergusonite structure at 10 GPa, and a second one at 17 GPa to an unresolved structure. Theoretical work has proposed either *M*- or *M'*-fergusonite as the second structural phase, and wolframite or a $P2_1/c$-symmetry structure as the third. In this *ab initio* study, we find that the *M'*-fergusonite structure is a better candidate for the second phase of $YLiF_4$, and propose a new structure with *Cmca* symmetry as the third.

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## I. GENERAL REMARKS

$YLiF_4$ is an ambient pressure tetragonal scheelite [space group (SG) $I4_1/a$, no. 88] material, used in the industry as a laser host for trivalent rare-earth ions. It has received considerable attention in recent years and several experimental and theoretical studies under pressure have been published.[1–10] Recent experimental works under high pressure have found that $YLiF_4$ undergoes a reversible phase transition around 10 GPa from the scheelite to the fergusonite structure,[1,3–5] as identified by x-ray diffraction (XRD) measurements.[5] Furthermore, another phase transition has been observed at 17 GPa, but the final structure could not be completely characterized.[5] On the other hand, Raman and photoluminescence (PL) anomalies, which seem to bear no correlation with identified phase transitions by XRD measurements, have been measured in the 5–7 GPa range of pressures.[1–4]

The high-pressure phase transitions in $YLiF_4$ have also been studied recently from the theoretical side.[6–8] Molecular dynamics (MD) simulations of Sen *et al.* show a first phase transition from scheelite to *M'*-fergusonite (SG $P2_1/c$, no. 14) at a low pressure of 6 GPa, and a second one at 16 GPa to another structure with the same symmetry as the *M'*-fergusonite structure.[6] *Ab initio* calculations in the framework of the density functional theory (DFT) performed by Li *et al.* agreed with the experimental observation of a scheelite to fergusonite (SG $C2/c$, no. 15) transition at 10 GPa, and then suggested a second transition to the wolframite structure (SG $P2/c$, no. 13) at 17.6 GPa.[7] Finally, recent *ab initio* calculations also in the framework of the DFT performed by Minisini *et al.*, found as second stable phase the *M'*-fergusonite, though the pressure in this first phase transition was overestimated by ~6 GPa.[8]

Theoretical explanations for the Raman and PL anomalies have been presented by several authors. Errandonea *et al.*[9] tentatively assigned the anomalies to a transformation between two scheelite polytypes differing in the setting angle. They made this assignment on the basis of the assumption that the $LiF_4$ tetrahedra in the scheelite structure remain undistorted but rotate under pressure, as suggested by the experiments of Wang *et al.*[4] and the calculations of Sen *et al.*[10] A similar explanation was offered in Ref. 8. On the other hand, Sen *et al.*[6] considered that the anomalies could be indicative of the phase transition to the *M'*-fergusonite structure that they located around 6 GPa.

In this work we present an accurate *ab initio* DFT study of $YLiF_4$ under pressure. We first study the lower (up to the second transition) pressure range and find that the *M'*-fergusonite has a lower energy than *M*-fergusonite, and a structural behavior that may explain the experimentally observed anomalies. Then we study some of the structures that are, or have been proposed as, stable in the high-pressure range for $ABX_4$ compounds, and find that no one has lower energy than a new phase with *Cmca* symmetry that, to our knowledge, has not been studied before in this material.

## II. THEORETICAL CALCULATION DETAILS

Our *ab initio* calculations were performed with the VASP code,[11] using the projector augmented waves[12] (PAW) pseudopotentials supplied with the package,[13] within the generalized gradient approximation[14] (GGA) for the exchange and correlation energy. The improved tetrahedron method with Blöch corrections[15] was used for the Brillouin-zone integrations.

In order to achieve high-precision results, we used a plane-wave energy cutoff of 1300 eV, and a cutoff for the augmentation charges of 1500 eV. Together with fine *k*-point grids generated using a gamma-centered Monkhorst-Pack scheme, this assures a convergence of at least 2 meV per formula unit (f.u.) for the total energy of each structure considered, and 0.1 GPa for its pressure. These settings also guarantee a good comparison between the structures with the smallest primitive cells (only 12 atoms) and the biggest ones. We performed some calculations at the same volume per formula unit on the *M*-fergusonite structure represented as a $C2/c$ 12 atom primitive cell and as a $P2_1/c$ 24 atom 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 with a Birch-Murnaghan fourth-order equation of state[16] (EOS) 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

 

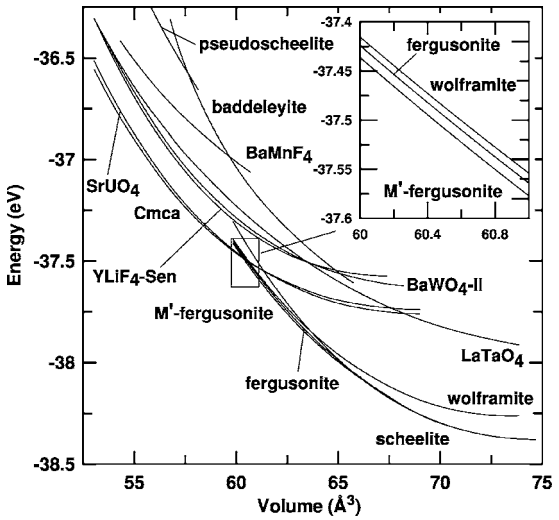


FIG. 1. Energy vs volume curves of the structures studied in this work. The structure labeled as $YLiF_4$-Sen is the high-pressure one found by Sen *et al.* in Ref. 6. The inset shows the energy of the fergusonite, $M'$-fergusonite, and wolframite structures in the area marked in the main figure. All extensive magnitudes are written per formula unit.

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.

## III. RESULTS

### A. Low-pressure phases, first structural transition

As candidates for being stable at low pressures, we have studied the scheelite (SG $I4_1/a$, no. 88, $Z=4$), $M$-fergusonite (SG $C21/c1$, no. 15, $Z=4$), and $M'$-fergusonite (SG $P2_1/c$, no. 14, $Z=4$) structures. Henceforward, the $M$-fergusonite structure will be called simply "fergusonite," and note that we have translated all the structural parameters from the $C21/c1$ standard setting to the $I12/a1$ setting for an easier comparison with the other structures.

Figure 1 shows the energy vs volume curves for the structures studied. It can be seen that both $M$- and $M'$-fergusonite structures have the same energy as the scheelite structure at low pressures. Furthermore, Fig. 2 shows that the two fergusonite structures reduce to the scheelite structure below 7.5 GPa, with their $a$ and $c$ lattice parameters equal to $a$ of scheelite, a $b$ parameter equal to $c$ of scheelite, and a monoclinic $\beta$ angle near 90°. Thus, we found scheelite as the stable structure of $YLiF_4$ at ambient conditions, in agreement with previous experimental and theoretical reports. Table I shows the structural parameters of our calculated scheelite structure and also the ones obtained experimentally, which are in reasonable agreement.

Table II summarizes the equilibrium volume per formula unit, the bulk modulus, and its first derivative for the scheelite structure compared to values from previous experimental and theoretical work. Our results for the low pressure phases are in reasonable agreement with previous theoretical works.[6–8]

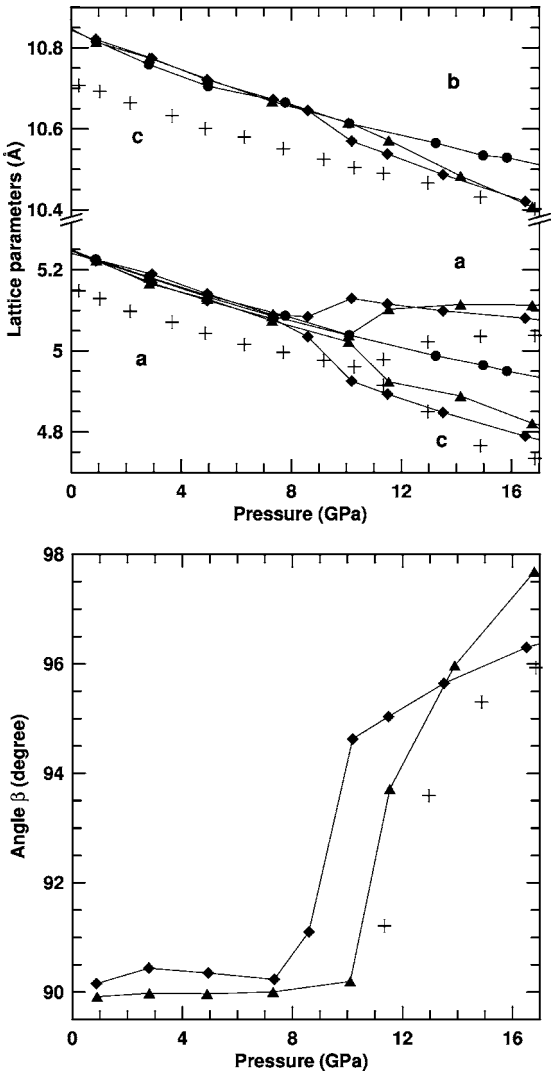


FIG. 2. (a) Pressure dependence of the $a$, $b$, and $c$ lattice parameters of the scheelite (circles), fergusonite (triangles), and $M'$-fergusonite (diamonds) structures. Experimental results after Ref. 5 (crosses) are also shown for comparison. (b) Pressure dependence of the $\beta$ monoclinic angle of the fergusonite (triangles) and $M'$-fergusonite (diamonds) structures. Note that in Ref. 5 the scheelite structure, which corresponds to a $\beta$ of 90°, was observed up to 10.6 GPa.

Upon increasing pressure, at 7.5 GPa the cell and internal parameters of the $M'$-fergusonite start to separate slowly from the scheelite ones, becoming completely different around 10 GPa (see Fig. 2). This is in agreement with the Sen *et al.* calculations which show the structural departure of $M'$-fergusonite from scheelite starting at 6 GPa.[6] However, Fig. 3 shows that there is no enthalpy difference between both phases until 11.6 GPa, so we can conclude that according to our calculations both phases coexists in a 4 GPa pressure range. Figure 4 shows the pressure dependence of the volume. The low volume change in the scheelite to $M'$-fergusonite transition, together with the previous results for the energy and structural parameters, classifies it as a second-order transition, in agreement with the experimental observations and previous suggestions.[3–6,17]

TABLE I. Lattice and internal parameters for selected pressures of the stable structures found in this work. Volume is written per formula unit. In the second column, the values in brackets are the ones quoted in Ref. 5 for the experimentally observed scheelite. In the next column we give in brackets the values of an $M'$-fergusonite cell constructed from the experimental parameters of the fergusonite structure given in Ref. 5 (see text).

| | Scheelite (SG $I4_1/a$, no. 88, $Z=4$) | $M'$-fergusonite (SG $P2_1/c$, no. 14, $Z=4$) | Cmca (SG *Cmca*, no. 64, $Z=8$) |
|---|---|---|---|
| $V$ (Å$^3$) | 67.38 [64.58] | 64.51 [62.51] | 56.76 |
| $P$ (GPa) | 10.1 [10.3] | 13.5 [13.3] | 19.5 |
| | | Lattice Parameters | |
| $a$ (Å) | 5.04 [4.96] | 5.10 [5.042] | 7.52 |
| $b$ (Å) | | 10.49 [10.42] | 12.34 |
| $c$ (Å) | 10.61 [10.50] | 4.85 [4.78] | 4.90 |
| $\beta$ (deg) | | 96.4 [95.28] | |
| | | Wyckoff Positions | |
| Y | (4*b*) (0, 0.25, 0.625) [(0, 0.25, 0.625)] | (4*e*) (0.254, 0.879, 0.017) [(0.25, 0.879, 0)] | (8*e*) (0.25, 0.146, 0.25) |
| Li | (4*a*) (0, 0.25, 0.125) [(0, 0.25, 0.125)] | (4*e*) (0.265, 0.347, 0.999) [(0.25, 0.362, 0)] | (8*f*) (0, 0.413, 0.208) |
| $F_1$ | (16*f*) (0.230, 0.586, 0.541) [(0.221, 0.581, 0.540)] | (4*e*) (0.395, 0.032, 0.749) [(0.430, 0.032, 0.756)] | (8*e*) (0.25, 0.326, 0.25) |
| $F_2$ | | (4*e*) (0.950, 0.302, 0.134) [(0.937, 0.296, 0.136)] | (8*f*) (0.0, 0.205, 0.458) |
| $F_3$ | | (4*e*) (0.891, 0.553, 0.282) [(0.930, 0.532, 0.256)] | (8*d*) (0.667, 0, 0) |
| $F_4$ | | (4*e*) (0.509, 0.777, 0.740) [(0.437, 0.796, 0.636)] | (8*f*) (0, 0.088, 0.069) |

A value of the transition pressure between 7.5 and 11.6 GPa is in agreement with the 10 GPa value obtained experimentally by Grzechnick *et al.*,[5] and also with the 9.3 GPa value obtained theoretically by Li *et al.*,[7] in both cases for a scheelite to fergusonite phase transition. It should be noted that, although we predict a transition to $M'$-fergusonite, the energy (see Fig. 1) and structural (see Table I) differences from fergusonite are rather small at low pressures. In Table I we give the structural parameters of our calculated $M'$-fergusonite at a pressure of 13.3 GPa, and the ones of a $M'$-fergusonite cell constructed from the experimental parameters of the fergusonite quoted in Ref. 5. This requires taking half of its $F_1$ ($F_2$) atoms at 8*f* Wyckoff positions and placing them under the $F_1$ ($F_2$) label of the $M'$-fergusonite, and the other half under the $F_3$ ($F_4$) label; a "true" $M'$-fergusonite cell could then be obtained by removing the condition of centering required by the space group of the fergusonite. Note that the calculated $M'$-fergusonite is very close to satisfying such centering condition. Figure 5 shows a detail of the $M'$-fergusonite structure of $YLiF_4$ at 13.5 GPa, according to the structural data of Table I.

According to our calculations, fergusonite becomes structurally different from scheelite at 10 GPa quite abruptly, with a noticeable enthalpy difference only above 13 GPa, and from there on remains about 15 meV per f.u. in energy above the $M'$-fergusonite. Such a small energy difference, which is however well above our precision of 1–2 meV per f.u., could perhaps disappear taking into account temperature effects (as indicated in Ref. 6). However, it should be noted that our results for the fergusonites agree with the ones obtained by Minisini *et al.*[8] We also think that the experimentally observed anomalies of the scheelite phase can be better explained on the basis of a scheelite to

TABLE II. Equilibrium volume per formula unit, bulk modulus, and its first derivative of the scheelite phase. We quote experimental (expt.) results from Ref. 5 and also theoretical ones from Refs. 6–8. US LDA stands for ultrasoft pseudopotentials within the local density approximation.

| | Ref. 5 Expt. | Ref. 6 MD | Ref. 7 US LDA | Ref. 7 PAW GGA | Ref. 8 PAW GGA | This work PAW GGA |
|---|---|---|---|---|---|---|
| $V_0$(Å$^3$) | 143.22 | 148.75 | 136.37 | 146.93 | 148 | 149.50 |
| $B_0$(GPa) | 81.0 | | 122.2 | 94.8 | 81 | 77.3 |
| $B'_0$ | 4.97 | | 4.97 | 4.97 | | 4.52 |

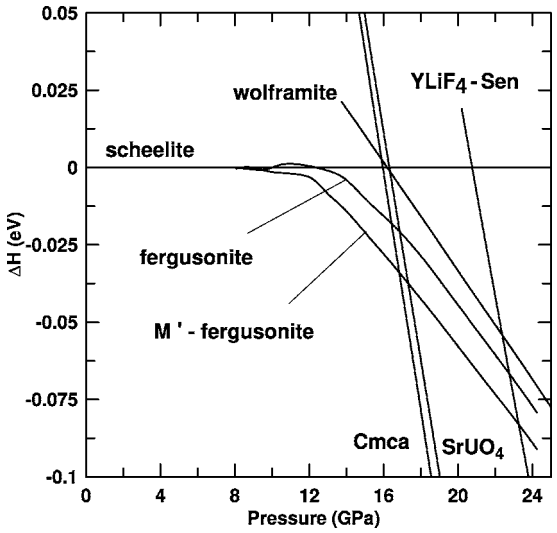


FIG. 3. Variation of enthalpy (per formula unit) with pressure. The enthalpy of the scheelite phase has been taken as reference. The stable postfergusonite structure proposed by Sen *et al.* in Ref. 6 is marked as $YLiF_4$-Sen.

*M′*-fergusonite slow phase transition such as the one proposed in this work.

The anomalies in the Raman shifts measured in $YLiF_4$ as a function of pressure in Refs. 2 and 4 are shown in Fig. 6(a). A clear change of pressure coefficient and the appearance of several modes are observed between 5 and 7 GPa, though the structure is still indexed as scheelite at those pressures.[5] Changes in the same pressure range are also observed in the frequencies of PL lines of $Eu^{3+}$ in $YLiF_4:Eu^{3+}$,[1] of $Nd^{3+}$ in $YLiF_4:Nd^{3+}$,[3] and of $Pr^{3+}$ in $YLiF_4:Pr^{3+}$.[4] These anomalies were explained as due to a rotation of the $LiF_4$ tetrahedra around the *c* axis of the scheelite structure (see Refs. 4, 9, and 10), which is responsible for the negative Grüneissen

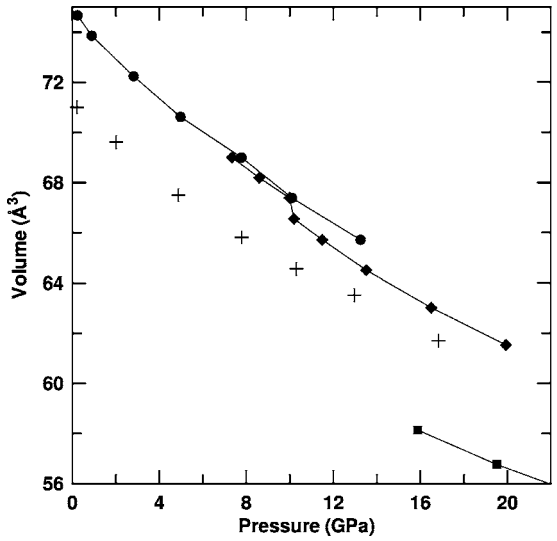


FIG. 4. Volume (per formula unit) vs pressure curves of the scheelite (circles), *M′*-fergusonite (diamonds), and Cmca (squares) structures. Experimental results after Ref. 5 (crosses) are also shown for comparison.

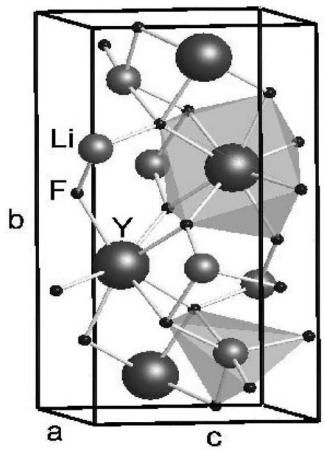


FIG. 5. Conventional unit cell of the *M′*-fergusonite structure found stable in this work at pressures between 7.5 and 16 GPa.

parameter of the lowest transversal $T(E_g)$ mode, related to the vibration of adjacent $LiF_4$-$LiF_4$ tetrahedra in the *x*-*y* plane perpendicular to the tetragonal *c* axis. A similar explanation was offered in Ref. 8 where this instability has been also associated to a change of the elastic constants. This rotation of $LiF_4$ tetrahedra in the *x*-*y* plane perpendicular to the tetragonal *c* axis was viewed in Ref. 9 as a polytype transformation without change in symmetry between different scheelite polytype structures.

In this work, we point out that these anomalies can be associated with the progressive transformation of the scheelite into the *M′*-fergusonite structure during the pressure range of coexistence of both structures between 7.5 and 11.6 GPa. This conclusion is in agreement with that of Sen *et al.*,[6] who related the anomalies to the beginning of the phase transition at 6 GPa. As suggested by Wang *et al.*,[4] a stiffening of the Li-F first-neighbor distance above 6 GPa is not enough for a change in the pressure coefficients of the Raman and PL modes. We have found that there is indeed a small stiffening of the first Li-F bond distance in the *M′*-fergusonite phase [see Fig. 6(b)]. Furthermore, Fig. 6(b) shows that there is also a noticeable decrease of one of the second-near-neighbor Li-F distances with increasing pressure, which is 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. We think that these changes above 7.5 GPa, plus the opening of the $\beta$ angle, shown in Fig. 2(b), are the cause of the change of pressure coefficients of the Raman mode observed experimentally between 6 and 10 GPa. They can also explain the change of the frequency pressure coefficient and frequency shift of the PL peaks of $Nd^{3+}$ observed experimentally, since this change of the second Li-F neighbors also affects the Y environment. In particular, the transformation of scheelite to *M′*-fergusonite does not affect the average coordination of Y, but the monoclinic distorsion destroys the $S_4$ symmetry of its site, thus lowering its symmetry. The same changes here summarized are also observed in the fergusonite, but at a higher pressure of 10 GPa which does not fit with the pressure at which the anomalies are experimentally observed.

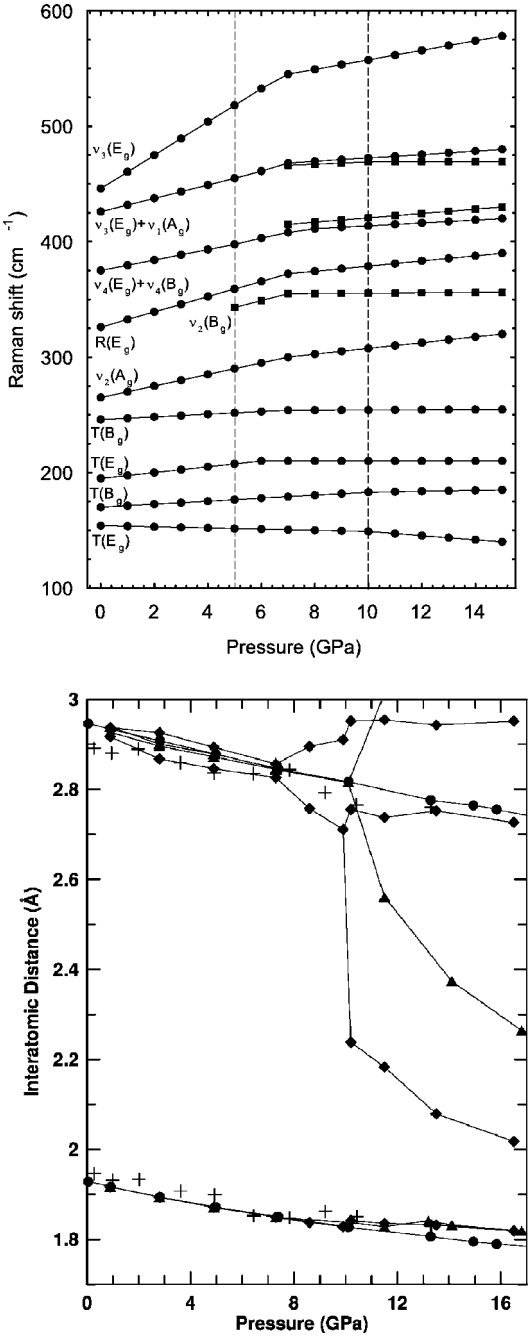


FIG. 6. (a) Pressure dependence of the Raman shifts in $YLiF_4$ at 300 K, after Refs. 2 and 4. Changes of the frequencies between 5 and 7 GPa are evident. (b) Evolution with the pressure of the interatomic distances below 3 Å between Li and F neighbors in the scheelite structure (circles), *M*-fergusonite (triangles), and *M′*-fergusonite (diamonds). Experimental results after Ref. 5 (crosses) are also shown for comparison.

### B. High-pressure phases, second transition

For the high-pressure range, we have studied some structures that have been experimentally observed or theoretically proposed as stable in $ABX_4$ compounds: wolframite (SG $P2/c$, no. 13, $Z=2$), which was found stable above 17.6 GPa in the *ab initio* calculations of Ref. 7; $YLiF_4$-Sen (SG $P2_1/c$, no. 14, $Z=4$), as we call the structure obtained by molecular dynamics simulations at pressures above 16 GPa in Ref. 6; baddeleyite (SG $P2_1/c$, no. 14, $Z=2$) and pseudoscheelite (SG *Pnma*, no. 62, $Z=4$), both proposed as high-pressure candidates in Ref. 9; $LaTaO_4$ (SG $P2_1/c$, no. 14, $Z=4$) and $BaMnF_4$ (SG $Cmc2_1$, no. 36, $Z=4$), observed in some rare earth tantalates;[18,19] the $BaWO_4$-II structure (SG $P2_1/n$, no. 14, $Z=8$), a high-pressure and -temperature phase observed in $BaWO_4$;[20] and the ambient-pressure structure of $SrUO_4$ (SG *Pbcm*, no. 57, $Z=4$), which has orthorhombic symmetry.[21]

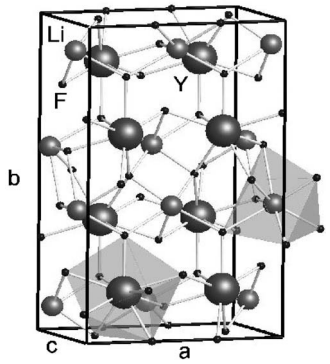


FIG. 7. Conventional unit cell of the structure with *Cmca* symmetry found stable in this work at high pressures.

We have also analyzed another structure which we call Cmca, after its space group. As can be seen, there are many entries in this and the previous (low-pressure) list of structures that are minima of the no. 14 space group, with four formula units in the unit cell and atoms at 4*e* Wyckoff positions (this is the case, for example, of the $LaTaO_4$ type or even of scheelite, which can be easily represented this way). Using different structural configurations as starting points for relaxation processes, we were able to find other minima of this space group. Among them, we found one with lower energy in the high-pressure range than any other of the structures already mentioned. Further analysis of this structure showed that it no longer belonged to the no. 14 space group, but to one of its supergroups: the orthorhombic *Cmca*, no. 64.

The energy vs volume curves represented in Fig. 1 show that the Cmca and $SrUO_4$-type structures are very close, though the Cmca has lower energy at the lower volumes. The enthalpy vs pressure curves in Fig. 3 again show the $SrUO_4$ and Cmca phases to be very close. However, Cmca has lower enthalpy at high pressures (15 meV per f.u. at 17 GPa), and we predict a transition from *M′*-fergusonite to Cmca at 16.8 GPa, in excellent agreement with the value of 17 GPa given by Grzechnick *et al.*[5] As shown in Fig. 4, the volume change in the *M′*-fergusonite to Cmca first-order transition is 7.9%. Full structural data for this phase are given in Table I for a pressure of 19.5 GPa.

Figure 7 shows the conventional unit cell of the Cmca structure at 19.5 GPa. It contains eight formula units, with Y atoms at 8*e*, Li atoms at 8*f*, and F atoms at 8*d*, 8*e*, and $(2\times)8f$ Wyckoff positions. It has orthorhombic symmetry like the $SrUO_4$, pseudoscheelite, and $BaMnF_4$ structures. With the exception of pseudoscheelite, which is found in several $A^{I}B^{VII}O_4$ compounds like $KClO_4$ and $CsReO_4$, these

structures with a high coordination of both $A$ and $B$ cations are not very common in $ABO_4$ compounds.[22,23] They are more common in $AB_2O_4$ compounds like $CuNd_2O_4$, $CuLa_2O_4$, $NiLa_2O_4$, $BaFe_2O_4$, $BaCo_2O_4$, and $BaNi_2O_4$, and in $ABX_4$ fluorites like $BaCuF_4$, $BaZnF_4$, $BaNiF_4$, $BaFeF_4$, and $BaCoF_4$. Furthermore, an orthorhombic structure with the same space group as $BaMnF_4$ has been observed as a high-temperature modification of $LaTaO_4$.[24] It should also be noted that the space group of the Cmca structure (no. 64) is a supergroup of the space groups of the $M'$-fergusonite and $SrUO_4$ structures (nos. 14 and 57, respectively).

The cationic arrangement of the Cmca structure can be obtained from the $M'$-fergusonite structure in a simple manner. Looking at the $M'$-fergusonite conventional cell from the $c$ axis, with the $b$ axis pointing upward, there are two cations of Y (or Li) in the upper half of the cell, and another two in the lower half. The atoms paired this way are more or less one above the other. If the uppermost and lowermost atoms are displaced along the plane perpendicular to the $b$ axis in $\sim(0.5,0,0.5)$, the cationic arrangement of the Cmca is obtained. In this structure there are two zig zag chains of Y (or Li) atoms, one above the other when looking from the $c$ axis with the $a$ axis pointing upward, and the cations are aligned one above the other when looking from the $a$ axis.

In this Cmca structure, the coordination of cations with F is nine for Y, and 6+1 for Li. At 19.5 GPa, there are nine F atoms at distances between 2.2 and 2.5 Å from the Y cation, with the next ones at distances greater than 3 Å; for the Li atoms, there are six F neighbors at distances between 1.8 and 2.2 Å, another one at 2.4 Å, and the rest at distances greater than 2.8 Å. This cationic coordination is very similar to that of the $SrUO_4$ structure, in which we found each Y cation surrounded by nine F atoms at distances between 2.2 and 2.5 Å, and each Li with six F neighbours at 1.8–1.9 Å, for a pressure of 20.3 GPa.

The high-pressure phase transformation from the $M'$-fergusonite structure to the Cmca structure leads to an increase in both cation coordination numbers. This behaviour is expected on the basis of the decrease of ionic radii with increasing pressure.[23,25] Following this argument, the decrease of Y ionic radius would lead to an increase of the Y cation coordination from eight in $M'$-fergusonite to nine in Cmca, and the decrease of Li ionic radius would lead to an increase of the Li cation coordination from 4+1 in $M'$-fergusonite to 6+1 in Cmca. In the Cmca structure, each Li cation has a similar coordination to the one it has in the wolframite, $LaTaO_4$, and $BaWO_4$-II structures observed in other $ABX_4$ compounds at high pressures. It should be noted that it was speculated by Grzechnick *et al.*[5] that the unresolved high-pressure phase of $YLiF_4$ could have a coordination around six. Finally, we have also found this orthorhombic structure with Cmca symmetry stable at high pressures in other $ABX_4$ compounds, namely, $SrWO_4$ and $CaWO_4$,[26] and $PbWO_4$ and $BaWO_4$.[27]

The high-pressure phase transition series leading from the scheelite to the $M'$-fergusonite and then to the Cmca structure in $YLiF_4$ can be rationalized on the basis of Bastide's diagram.[23] In this diagram, the $ABX_4$ compounds are positioned according to their ionic radius ratios $r_A/r_X$ and $r_B/r_X$, so that $YLiF_4$ would be in the limit of eight coordination for Y and four coordination for Li ($r_Y/r_F=0.78$ and $r_{Li}/r_F=0.45$). With increasing pressure, the normal behavior of compounds (i.e., if steric stresses between cations are small[9]) is to adopt more compact structures with larger $r_A/r_X$ and $r_B/r_X$ ionic radius ratios according to the north-east (N-E) rule displacement in Bastide's diagram. In particular, $NaCrF_4$ ($r_{Na}/r_F=0.91$ and $r_{Cr}/r_F=0.48$) is a fluoride that is in direction N-E with respect to $YLiF_4$ and has the $M'$-fergusonite structure at ambient conditions.[28] $SrUO_4$ ($r_{Sr}/r_F=0.97$ and $r_U/r_F=0.69$) is also in the direction N-E with respect to $YLiF_4$ and, as already mentioned above, features the same orthorhombic symmetry as Cmca and very similar first-neighbor coordination numbers. Therefore, the phase transitions of $YLiF_4$ under pressure follow reasonably well the N-E rule in Bastide's diagram. We have to note that we have used Shannon's ionic radii to calculate the ionic radius ratios.[29] We also have to note that a feature of the change in coordination of the $B$ cation from four to seven in these phase transitions from scheelite to Cmca is that there is a small increase of the $r_B/r_X$ ionic radius ratio when going from scheelite to $M'$-fergusonite, whereas there is a big increase of the $r_B/r_X$ ionic radius ratio when going from $M'$-fergusonite to Cmca. These different changes could be likely related to the second-order class of the scheelite to $M'$-fergusonite phase transition and the first-order class of the $M'$-fergusonite to Cmca phase transition.

For the other structures we found that wolframite remains 20–30 meV per f.u. in energy above $M'$-fergusonite in all the volume range studied. This result is in agreement with Ref. 8, which also found wolframite unstable against the $M$- and $M'$-fergusonites. In Ref. 7, the $M'$-fergusonite structure was not considered, so this is likely the main reason for the disagreement between our results. Without taking into account Cmca, our calculations show that $YLiF_4$-Sen structure (also a minimum of space group no. 14, with F coordination of ten and eight for Y and Li, respectively) would become stable at a pressure of 23.3 GPa, followed by the $LaTaO_4$-type structure at 33.5 GPa. Also note that the $BaWO_4$-II structure is very close in energy to $YLiF_4$-Sen at high pressures. The use of the GGA approximation for the exchange-correlation energy and/or the lack of temperature effects in our work, may be the causes of the higher pressure transition from $M'$-fergusonite to $YLiF_4$-Sen as obtained in our work vs the one found in Ref. 6, which nevertheless used a completely different calculation method. In any case, it should be noted that in our calculations the Cmca phase is much lower in enthalpy than the other structures proposed as stable around 17 GPa, so even if the calculation method can be improved, it is likely that this structure will remain competitive in the high-pressure range.

## IV. 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, we found this material crystallized in a scheelite structure, in agreement with previous experimental and theoretical works.

Upon increasing pressure, we find that $M'$-fergusonite has lower energy and enthalpy than the experimentally proposed

fergusonite. A stable $M'$-fergusonite around 10 GPa is in agreement with molecular dynamics[6] and recent DFT calculations,[8] and was not considered in other DFT calculations,[7] which proposed the fergusonite as stable. Thus, we propose the $M'$-fergusonite (SG no. 14) instead of the fergusonite (SG no. 15) as the second stable phase of $YLiF_4$, though it should be noted that the structural differences between the two are rather small.

We also find that the scheelite to $M'$-fergusonite transition may be responsible for the anomalies observed in the Raman and PL spectra of scheelite above 5 GPa. The anomalies are likely due to the changes in the interatomic distances and symmetries under pressure in this slow, second-order phase transition.

In the high-pressure range, we propose a new structure with *Cmca* symmetry as the stable one. Our results for this phase, not previously considered in any other work to our knowledge, show that it is much lower in energy than the other two proposed in previous theoretical works (i.e., $YLiF_4$-Sen by Sen *et al.*[6] and wolframite by Li *et al.*[7]), while it is close to the ambient-pressure structure of $SrUO_4$, with which it shares some features. Although this Cmca structure has not been observed experimentally, the transition pressure of ~17 GPa and the first-neighbor coordination numbers are in agreement with our current knowledge of the high-pressure behavior of $YLiF_4$, and of $ABX_4$ compounds in general. However, it should be noted that we have studied a limited number of structures, so we cannot exclude the appearance of other stable ones at high pressures. Further experimental work may be needed to completely determine the third structure adopted by this compound under compression.

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