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Wolframite: the post-fergusonite phase in YLiF₄

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Abstract

By means of electronic structure calculations, we have studied phase transitions in YLiF₄ using the Vienna *ab initio* simulation package (VASP) within the generalized gradient approximation (GGA) and the local density approximation (LDA). The scheelite to fergusonite phase transition takes place at 9.3 GPa with a 0.5% volume collapse. By comparing the total energy difference for several possible post-fergusonite structures, BaWO₄(II) type, LaTaO₄ type, BaMnF₄ type and wolframite type, we propose that the wolframite-like structure is the most likely new phase for the second phase transformation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Yttrium lithium tetrafluoride is a promising host material for rare-earth ion lasers. YLiF₄ belongs to space group *I*4₁/*a* and crystallizes in the tetragonal scheelite-type structure at ambient conditions. The cations Y³⁺ and Li¹⁺ are coordinated by eight and four fluorine atoms, respectively. The bonding inside LiF₄³⁻ is assigned to be ionic in character.

During the last decade, a large number of investigations have been carried out regarding crystallographic phase transitions under pressure. Fluorescence experiments for YLiF₄ were carried out by Liu *et al* [1] at room temperature up to 15 GPa and a reversible phase transition was reported in the pressure range from 10.0 to 10.5 GPa. However, the high pressure phase could not be determined due to the limitations of the experiment. Two years later, Sarantopoulou *et al* [2] studied a single crystal of YLiF₄ using Raman scattering measurements in the pressure range 0–20 GPa at room temperature and an abrupt change in the phonon frequency was observed at 7 GPa, which indicates a phase transformation due to a stiffening of LiF₄³⁻ group, but no other phase transitions were reported above this pressure. Later on, a luminescence experiment on 2% Nd-doped YLiF₄ showed subtle structure changes of the scheelite structure around 5.5 GPa, but the major spectral changes were observed near 10 GPa [3]. So the possibility of a transition from scheelite to fergusonite was predicted.

Recently, Grzechnik *et al* [4] have identified that the high pressure phase present above 10 GPa is of fergusonite type. Moreover, a second phase transition near 17 GPa was detected. However, the structure of the post-fergusonite phase was not determined, but it was suggested to be of a monoclinic type with a B coordination number higher than four.

The lack of knowledge of the new second high pressure phase motivated us to undertake a thorough theoretical investigation of YLiF₄ at high compression. Utilizing density functional theory based on the generalized gradient approximation as well as the local density approximation, we confirmed the first scheelite to fergusonite phase transition at 9.3 GPa and proposed the second new high pressure phase by total energy calculations.

2. Calculation details

We studied the crystallographic structures of YLiF₄ using the Vienna *ab initio* simulation package (VASP) and the projector augmented wave (PAW) [8] method. The calculations of geometry optimization and phase stability were performed by means of the generalized gradient approximation (GGA) [9] based on the density functional theory (DFT). The local density approximation (LDA) [7, 10] together with ultra-soft Vanderbilt type pseudopotentials [5, 6] was used to compare with the GGA calculations. High precision calculations with a cut-off energy of 500 eV for the plane-wave basis were performed. The Brillouin zone integration was carried out using the special *k*-point sampling of the Monkhorst–Pack type. The total energies were converged to below 0.001 eV as regards the number of *k*-points. The tetrahedron method with Blöchl corrections was applied for both geometry relaxation and total energy calculations. The geometry optimization was considered to be converged when the total force on the atoms was less than 1.0×10^{-3} eV Å⁻¹.

3. Results and discussions

In our calculation, YLiF₄ shows two phase transitions:

- (1) from scheelite to fergusonite at 9.3 GPa, with 0.5% volume collapse—such a small volume discontinuity may be hard to detect experimentally;
- (2) from fergusonite to the wolframite-like structure at 17.6 GPa, with 2% volume collapse. The larger volume collapse compared with the former transformation is associated with a change of coordination number.

The equilibrium volumes are fairly close for scheelite and fergusonite structures, 293.9 and 292.6 Å³, respectively (table 1). The total free energy difference for these two phases is only 3 meV/atom at ambient pressure. The calculated bulk modulus and the density of states (DOS) at ambient conditions also show close similarities between these two phases. The very good agreement between the theoretical and experimental transition pressures, 9.3 GPa compared with 10.6 GPa, demonstrates the accuracy of state-of-the-art electronic structure calculations.

It is still unknown to which phase the fergusonite phase transforms at 17 GPa; we took the BaWO₄(II)-type [11], LaTaO₄-type [12], BaMnF₄-type [13] and wolframite structure proposed by Grzechnik *et al* [4] as high pressure candidates. All internal parameters have been optimized around the transition pressure. By comparing the total free energy at a volume of 253.92 Å³ (20 GPa), we can exclude the BaWO₄(II) type (*P*2₁/*n*, *Z* = 8) and BaMnF₄ type (*Cmc*2₁, *Z* = 4) from further considerations. The LaTaO₄-type (*P*2₁/*c*, *Z* = 4) or the NiWO₄-type wolframite (*P*2/*c*, *Z* = 2) structures are very close in energy to the fergusonite phase, so these two phases could be possible candidates at high pressure. Full optimization

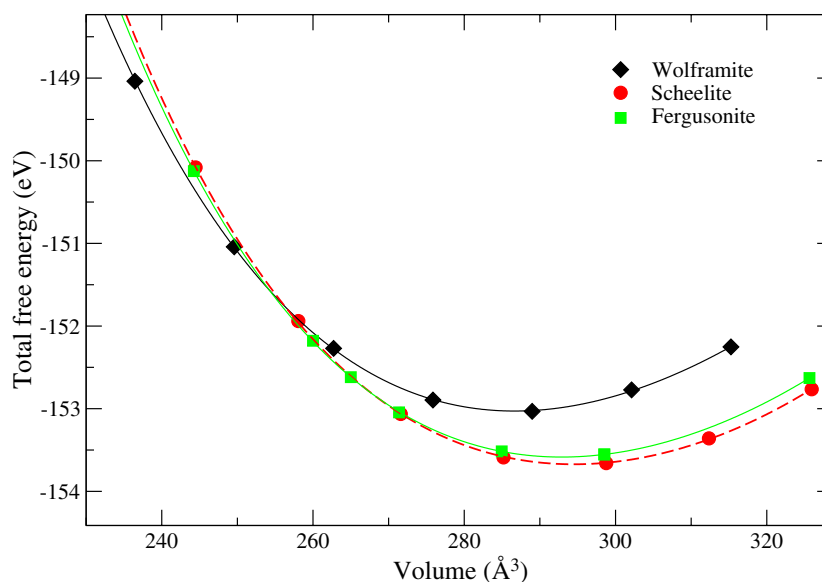


Figure 1. The total energy difference as a function of volume (24 atoms) for the three different crystal structures for YLiF₄: scheelite, fergusonite and wolframite-like. The scheelite–fergusonite phase transition takes place around the volume 268 Å³ and the transition volume of fergusonite–wolframite is around 254 Å³.

Table 1. Comparison between experiment and theory. V_0 (Å³) is the equilibrium volume, B_0 (GPa) is the bulk modulus at ambient pressure and B'_0 is the first pressure derivative of the bulk modulus.

	Scheelite Experiment	Scheelite		Fergusonite		Wolframite-like	
		LDA	GGA	LDA	GGA	LDA	GGA
a	5.145(1) ^a	5.086	5.202	5.153	5.276	4.877	4.989
b				10.625	10.884	5.269	5.432
c	10.820(5) ^a	10.544	10.859	4.961	5.104	5.180	5.308
β				93.490	93.197	94.994	94.962
V_0	286.440(9)	272.746	293.853	271.114	292.636	132.605	143.309
B_0	81 ± 4 ^b	122.2	94.8	122.5	95.3	127.1	97.8
B'_0	4.97 ± 0.68 ^b	4.97	4.97	4.97	4.97	4.97	4.97

^a Reference [15].

^b Reference [14].

has been performed for these two structures to look for their energy minima. A high precision calculation has been performed to compare their total free energy differences. The optimized wolframite phase is computed to be more stable in the pressure range we have studied, as shown in figure 1. The relaxed atomic positions of the wolframite-like structure are shown in table 2. The equilibrium volume, bulk modulus and the first pressure derivative of the bulk modulus for these phases were derived through fitting the Birch–Murnaghan equation of state (EOS), as shown in table 1. The calculated scheelite equilibrium volume is 3% overestimated compared with the experimental data. A calculated bulk modulus of 94.8 GPa agrees well with the experimental value of 81 GPa for the scheelite structure. Here B'_0 has been fixed to the experimental value of 4.97 for comparison.

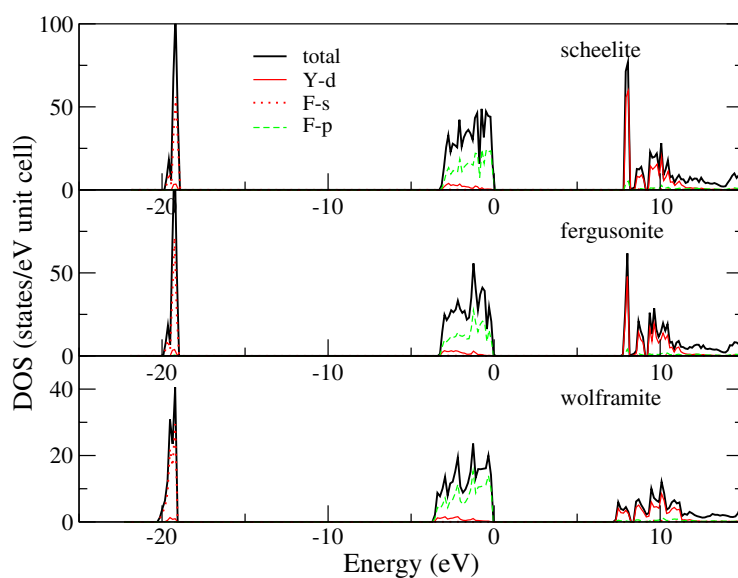


Figure 2. Calculated density of states (DOS) for scheelite, fergusonite and wolframite-like structures. The Fermi level is set to 0 eV.

Table 2. The atomic positions of the wolframite-like structure in YLiF_4 .

Atom	Site	x		y		z	
		LDA	GGA	LDA	GGA	LDA	GGA
Y	2f	0.5	0.5	0.7361	0.7441	0.25	0.25
Li	2e	0	0	0.1827	0.2040	0.25	0.25
F1	4g	0.2497	0.2516	0.0517	0.0610	0.0217	0.0382
F2	4g	0.2634	0.2535	0.4182	0.4301	0.3931	0.4116

In comparison with the GGA calculations, we also show the LDA results in table 1. Note that the LDA always tends to overestimate the bonding. This will in turn underestimate the volume, but at the same time overestimate the bulk modulus. GGA gives an improvement of the LDA. When LDA is replaced by GGA, the equilibrium volume, bulk modulus and transition pressure are much closer to the experimental data.

We compared the GGA and LDA calculated electronic density of states (DOS) and found a closely related behaviour between them. The LDA calculated DOSs for scheelite, fergusonite and wolframite-like structures are shown in figure 2. A sharp peak located around -20 eV coming from F 2s states is separated from the top of the valence band by a huge 16 eV gap. The upper valence band (UVB) is dominated by F p and mainly located between -3.3 and 0 eV. The conduction band (CB), composed by Y d states, is separated from the UVB by a wide bandgap of 8 eV. The wolframite-like structure has a little wider calculated UVB band width than the scheelite and the fergusonite structures. The peak located around 8 eV in both scheelite and fergusonite structures does not exist in the wolframite-like structure.

The crystallographic transformations in YLiF_4 should be primarily mediated through a change of coordination of the LiF_4^{-3} group [2]. In YLiF_4 , the Li–F bond is more ionic and thus more compressible than the Y–F bond [16]. At ambient pressure, each Li site is surrounded by four equivalent F sites to form a tetrahedron, with the first nearest neighbour distance

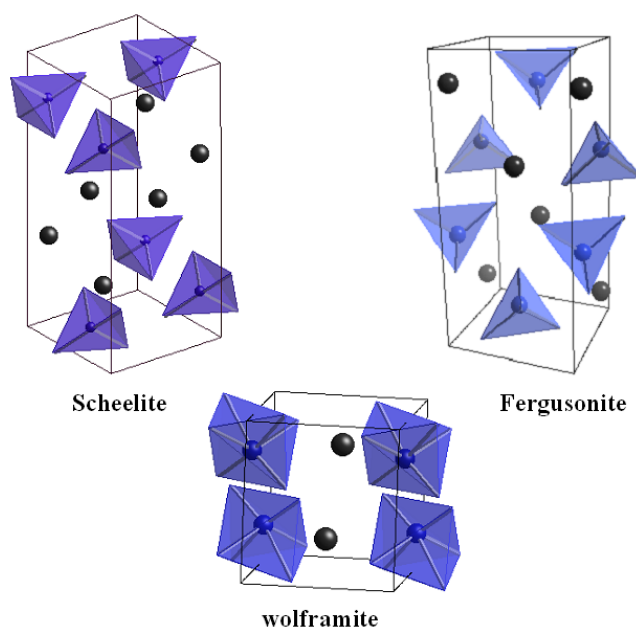


Figure 3. Scheelite, fergusonite and wolframite-like crystallographic structures. The Y atoms are represented by the solid black balls. Li atoms are inside the tetrahedral cages in the scheelite and fergusonite structures and in octahedral cages in the wolframite structure.

of 1.94 Å and the second nearest neighbour distance 2.89 Å. After the transformation to the fergusonite structure, the Li–F nearest bond distance and its second nearest neighbour distances are 1.83–1.89 and 2.76–2.78 Å respectively [4]. Therefore, the tetrahedra are still isolated but somewhat deformed. From figure 3, we can see that the high pressure fergusonite phase is nothing but a distorted scheelite-type structure. After the second phase transition to the wolframite-like structure, the Li–F tetrahedral cages are totally deformed. The coordination of the Li⁺¹ is six compared to four in the fergusonite structure. However, the modified wolframite structure has cation coordination 8–6 instead of 6–6 in the ideal wolframite structure. At transition pressure, the Y–F bond distances are 2.19, 2.20 and 2.21 Å to six sites and 2.24 Å to two additional sites, and the Li–F bond distances are 1.83 to four sites and 2.27 to two other sites.

It is commonly observed that the coordination increases with increasing pressure. The high pressure wolframite-like structure is more close packed than either the scheelite or fergusonite structures, with cation coordination 8–6 compared to 8–4 in both of them. Scheelite–wolframite transition has been observed in a number of ABO₄ compounds, such as CaWO₄ [17], which shows a scheelite–wolframite structure change around 12 GPa. Accordingly, one could therefore regard the fergusonite structure as an intermediate phase between scheelite and the more condensed wolframite-like structure in YLiF₄.

4. Conclusion

We have studied the crystallographic phase transitions in YLiF₄ by means of *ab initio* calculations. Two pressure induced transitions were found theoretically: from the scheelite structure to the fergusonite structure at 9.3 GPa and from the fergusonite structure to a

wolframite-like structure at a pressure of 17.6 GPa. The high pressure wolframite-like phase has the monoclinic structure, with Y^{+3} coordination 8 and Li^{+1} coordination 6. We hope our work will stimulate further experimental study of the high pressure post-fergusonite phase in $YLiF_4$.

Acknowledgments

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