Ab-initio investigations of LuLiF$_4$ compound under pressure

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Abstract. We have performed ab-initio calculations for the structural and mechanical properties of sheelite compound LuLiF$_4$ under pressure. A good agreement with experimental results has been obtained.

1. Introduction

A great progress has been done in the last years in the study of pressure-effects on the structural and mechanical properties of sheelite compounds MLiF$_4$, where M stands for lanthanides [1]. These compounds have the CaWO$_4$-type or scheelite-type structure which is a superstructure of fluorite CaF$_2$ (Fm3m, Z = 4). The fluorine atoms are situated in a distorted simple cubic arrangement and the Li$^{1+}$ and M$^{3+}$ cations are fourfold and eightfold coordinated by fluorines, respectively.

The interest to the LuLiF$_4$ compound was invoked by the fact that this material possesses the own electrical dipole moment in some temperature range. LuLiF$_4$ structure has been investigated using synchrotron angle-dispersive x-ray powder diffraction in a diamond anvil cell at high pressures and room temperature [2]. The authors investigated structural and mechanical data that allows us to compare our results with experimental one.

Earlier Minisini et al. [3] have studied thermo-mechanical properties of LuLiF$_4$sheelite at ambient pressure by means of density functional theory (DFT) was performed. Particularly, elastic stiffness coefficients of LuLiF$_4$ sheelite have been estimated by stress–strain method.

2. Calculation parameters

We performed ab-initio calculations by means of DFT [4, 5] with using VASP 5.2 [6] (Vienna Ab-Initio Simulation Package), the part of the MedeA® interface. The exchange–correlation functional was approximated by the gradient corrected form proposed by Perdew-Burke-Ernzerhof[7]. The electronic degrees of freedom were described using the projector augmented wave method and basis of plane waves [8, 9].

Based on the results obtained [10] only non magnetic method was considered and f-electrons of Lu were considered as the «kept frozen in the core». It was made due to the fact that taking into account spin degree of freedom makes no any essential influence on structural and mechanical parameters. During calculations we considered LuLiF$_4$ structure with symmetry I4$_1$/a and C12/c1, Z = 4 in the range of pressure from 0 to 20 GPa with step 2 GPa. Full optimization of the structure was performed until the maximum force dropped below 0.005 eV, whereas the self-consistent field convergence
criterion was set at $10^{-6}$eV. Next parameters have been chosen to obtain the converging results. A k-mesh is equal to $9^3$ for the structure with symmetry $I4_1/a$ and $7^3$ for the structure with symmetry $C12/c1$. For each k-point the wave functions were expanded in terms of plane waves until a cutoff energy of 796 eV for $I4_1/a$ structure and until 576 eV for $C12/c1$ structure. For forces and energy optimization Methfessel-Paxton scheme was used with smearing 0.12 eV for $I4_1/a$ structure and 0.17 eV for $C12/c1$ structure. The method of Methfessel-Paxton allows to describe very accurate the total energy of the system.

The structure optimization was made by three stages. The atom positions, shape and volume of cell can be changed at the first and second stages. At the third stage only atom positions can be changed.

It is well known that Lu has $4f^{14} 5d^{1} 6s^{2}$ electronic configuration. GGA (generalized gradient approximation) +U scheme was applied namely to d-electrons of Lu, because of f-orbital is completed. This method was used in order to treat strong correlation for d-electrons. Different Habbard parameters in the range from 1 to 3 eV were considered, but the most suitable parameter is equal to 1 eV.

For investigation mechanical properties Mechanical-Thermal (MT) module of VASP 5.2 was used. The calculation parameters were the same as above; the value of strain is 0.002.

3. Results

3.1 Structural properties

We performed the analysis of structural parameters of LuLiF$_4$ compound with two different symmetries $I4_1/a$ and $C12/c1$. The structure parameters ($a^{\text{im}}$, $b^{\text{im}}$, $c^{\text{im}}$, where t-tetragonal and m-monoclinic symmetries) and experimental points [2] versus pressure were plotted on the figure 1.

![Normalized lattice parameters](image)

**Figure 1.** Lattice parameters dependence on pressure normalized to the respective value at ambient pressure (experimental values: empty square- $c^T / c_0$, empty rhomb- $a^T / a_0$, empty triangle- $a^m / a_0$, empty inverse triangle- $b^m / b_0$, empty circle- $c^m / c_0$; *ab-initio* calculations: solid rhomb- $a^m / a_0$, solid square- $b^m / b_0$, solid circle- $c^m / c_0$).

We can see a good agreement with experimental results. *Ab-initio* calculations show that the structural parameters of LuLiF$_4$ with two symmetries are mostly the same below 10.5 GPa. It can be explained by the fact that $C12/c1$ is a subgroup of $I4_1/a$ symmetry. Two symmetries structural parameters diverge after 10.5 GPa.

The figure 2 presents the angle $\beta$ (between a and c axes) dependence on pressure for LuLiF$_4$ structure with $C12/c1$ symmetry. This parameter also changes sharply at 10.5 GPa.
3.2 Mechanical properties
The behavior of unit-cell volumes of LuLiF$_4$ were investigated for two symmetries until 20 GPa. The corresponding figure is presented below:

\[
\begin{align*}
&V = \frac{3}{2}B_0 \left[ \left( \frac{V_0}{V} \right)^3 - \left( \frac{V_0}{V} \right)^5 \right] + \frac{3}{4} \left( B'_0 - 4 \right) \left( \frac{V_0}{V} \right)^5 - 1
\end{align*}
\]

(1)

As a result bulk modulus $B_0$ and equilibrium volume $V_0$ were evaluated. Also the values of equilibrium volume and bulk module were obtained by M-T module of VASP 5.2.

The results presented in the table 1 demonstrate a good agreement between the bulk module obtained by MT calculations, by Birch-Murnaghan (B-M) approximation and experimental results (B-M approximation of experimental data) [2].
Table 1. Equilibrium volume $V_0$, bulk modulus $B_0$, and the first pressure derivative of the bulk modulus $B'_0$.

| Methods | $V_0$, Volume, Å$^3$ | $B_0$, Bulk modulus, GPa | $B'_0$, The first pressure derivative of the bulk modulus |
|---------|----------------------|--------------------------|-----------------------------------------------------|
| B-M     | 283.4                | 83                       | 4.50                                                |
| MT      | 283.3                | 85                       | -                                                   |
| B-M experiment [2] | 280.7±0.2 | 85±3                     | 5.59±0.55                                           |

Table 2 presents the values of elastic stiffness coefficients obtained by MT calculations and the results obtained in the paper [3].

Table 2. Elastic stiffness coefficients (GPa) estimated by strain-stress method at 0 GPa.

| Elastic stiffness Coefficients, GPa | Paper [1] | MT calculations |
|------------------------------------|-----------|-----------------|
| $C_{11}$                           | 131       | 128             |
| $C_{12}$                           | 54        | 54              |
| $C_{13}$                           | 62        | 59              |
| $C_{16}$                           | 13        | 9               |
| $C_{33}$                           | 168       | 165             |
| $C_{44}$                           | 40        | 40              |
| $C_{66}$                           | 29        | 24              |

Shear module (38 GPa) and Young’s module (98 GPa) were obtained from the elasticity constants.

4. Conclusion

Thus, in this work we presented a density functional theory analysis of LuLiF$_4$ structure under pressure. A good agreement of structural parameters ($a$, $b$, $c$) for I4$_1$/a and C12/c1 symmetries with experimental results has been obtained. The values of bulk module and equilibrium volume obtained by MT calculations and by B-M approximation agree well with experimental results. The comparison of the elastic constants obtained by M-T module with relevant results of the paper [3] gives similar values.

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