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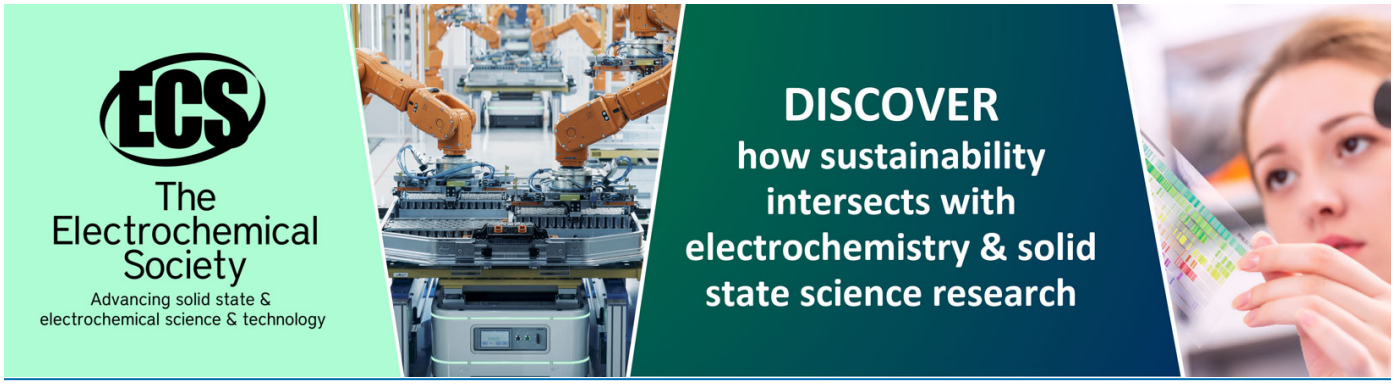

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Ab-initio investigation of $GdLiF_4$ structure under pressure

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Abstract. This work is devoted to the *ab-initio* studies of rare-earth double fluoride $GdLiF_4$ under external hydrostatic pressure. Structural and mechanical properties were considered by means of Vienna Ab-initio Simulation Program (VASP). A good agreement of lattice parameters and bulk modulus with experimental data has been obtained. The seven independent elastic constants of $I4_1/a$ $GdLiF_4$ structure were calculated from stress-strain method. The provideab-initio studies has revealed the instability of $GdLiF_4$ crystal structure above 10 GPa in accordance with available experimental findings.

1. Introduction

It has recently been concluded that pressure-induced post-scheelite (or post-fergusonite) structures in oxides, fluorides, and any otherABX_4-type compounds are not really well known [1]. That is why the investigation of high-pressure behaviour of $GdLiF_4$by measurements of its angle-dispersive x-ray powder diffraction patterns as a function of pressure was provided. Particularly the pressure-induced decomposition of $GdLiF_4$sheelite has been found.

The goal of the present paper is to study the evolution of structural and mechanical parameters with a pressure by means of *ab-initio* calculation and to compare the obtained dependencies with experimental data.

2. Calculations

$GdLiF_4$ is a sheelite compound.Scheelite crystals have a tetragonal $I4_1/a$ symmetry. It can be presented as dipyramidal pseudo-octahedra. In this structure, the primitive unit cell has two ABX_4 units.The crystal structure $GdLiF_4$ (see figure 1) can be described as highly ionic with Gd^{3+}cations and tetrahedral LiF_4 anions. Each Li^{1+}cation is surrounded by four equivalent fluorines in tetrahedral symmetry. Each Gd^{3+}cation shares corners with eight adjacent LiF_4 tetrahedra and the Gd^{3+}cations are surrounded by eight fluorines in approximately octahedral symmetry forming bisdisphenoids.

The crystallographic directions in $GdLiF_4$ consist of two equivalent directions (the a-axes), and one unique direction (the c-axis).

During the calculations we considered $GdLiF_4$ structure with initial lattice parameters (A= 5.235(1) Å, C= 11.01(2) Å, V= 302.0 $Å^3$) taken from the experiment [2].

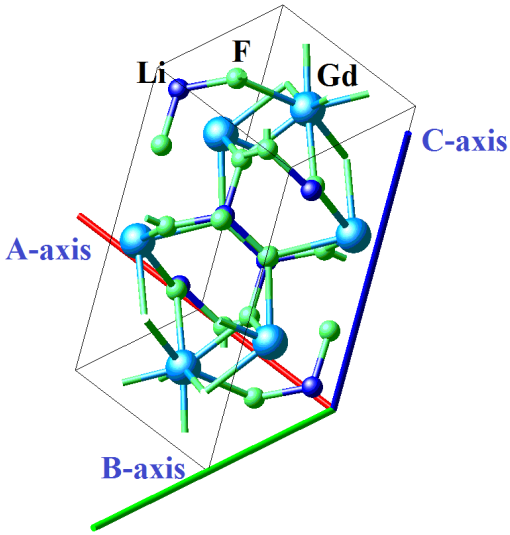

Figure 1. A tetragonal structure of $GdLiF_4$.

For numerical simulations we used Density Functional Theory [3, 4] as implemented in Vienna Ab-initio Simulation Package [5], part of MedeA© modelling interface. The exchange–correlation functional was approximated by the gradient corrected form proposed by Perdew-Burke-Ernzerhof [6]. The electronic degrees of freedom were described using the projector augmented wave method.

Three stages of structure optimization were performed in the range from 0 to 20 GPa with step 2 GPa. The atom positions, shape and volume of cell can be changed at first and second stages. At the third stage only atom positions can be changed. Such scheme of optimization was used for more accurate calculation of lattice parameters and energy of the structure. Full optimization of the structure was performed until the maximum force dropped below 0.002 eV/A^{-1} whereas the self-consistent field convergence criterion was set at 10^{-6}eV. A k-mesh of 0.5 $Å^{-1}$ leading to 12 symmetry-unique k-points was used to sample the Brillouin zone. For each k-point the wave functions were expanded in terms of plane wave until a cutoff energy 500 eV. To smooth the Fermi step function the Gaussian smearing with σ-parameter 0.1 eV was used.

Different methods were considered to investigate the influence of 4f-electrons on the structural and mechanical properties of $GdLiF_4$ structure. In this work non-magnetic, spin-polarized, spin-orbit coupling methods were used as well as the approximation that 4f-electrons of gadolinium are «kept frozen» in the core or are «included in the valence states».

3. Results

3.1 Structural properties

The obtained evolutions of the lattice parameters of $GdLiF_4$ as a function of pressure are presented on Figure 2 for different methods of taking into account the influence of f-electrons.

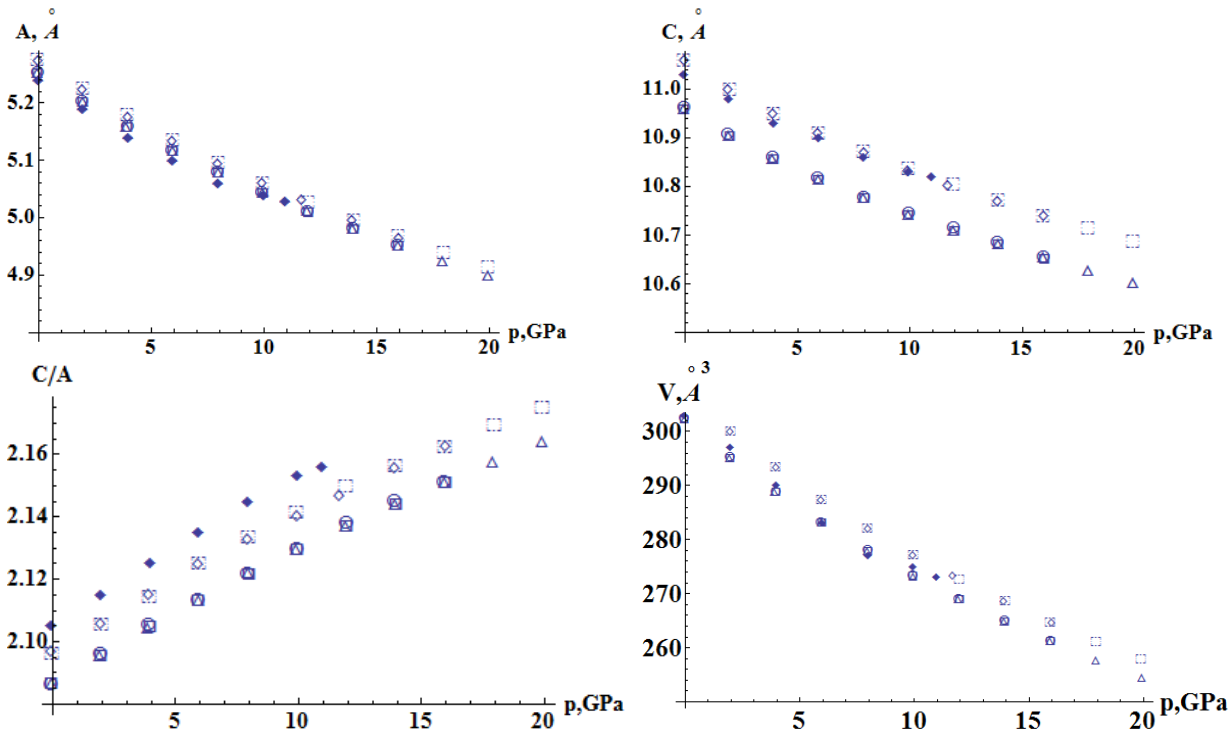

Figure 2.Evolution of structural parameter versus pressure for different methods of taking into account the influence of f-electrons (f-electrons are «kept frozen in the core»: non-magnetic state-empty square, spin-polarized state-empty triangle, spin-orbit -empty circle; f-electrons «included in the valence states»: spin polarized-chain line square, spin orbit-empty rhomb; experimental data [2]-solid rhomb).

The graphics demonstrate a good agreement between experimental results and calculated lattice parameters. Based on these results we can conclude thattaking into account spin degree of freedoms makes not too much influence on the structural parameters. The case of f-electrons «kept frozen in the core» gives the best agreement with experimental results for *A* parameter. A visible difference between the cases of f-electrons considered as a core and as a valence appears on pictures, which show the evolution of *C* lattice parameter and *C/A* axial ratio. As a pressure increases, the *C/A* ratio is increasing, indicating that the distortions in a crystal are enhanced at high pressures. The dependence obtained by case of f-electrons «included in the valence states» is closer to the experimental data. The analysis of volume evolution shows the best agreement with experimental data for the approximation when f-electrons are «kept frozen in the core». Since further we will be interested in the mechanical properties, we can restrict our consideration by the approximation of non-magnetic f-electrons «kept frozen in the core».

3.2 Mechanical properties

We have evaluated the elastic constants under pressure and have compared the values of bulk modulus and volume with experimental results. Mechanical-thermal analysis of $GdLiF_4$ was made by Mechanical-Thermal (MT) module of VASP 5.2 [7].

For a crystal belonging to the TII Laue group, the elastic stiffness constant matrix referred to the crystallographic axis (*X, Y, Z*) reference frame is

$$C_{ij} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & c_{16} \\ c_{12} & c_{22} & c_{13} & 0 & 0 & -c_{16} \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ c_{16} & -c_{16} & 0 & 0 & 0 & c_{66} \end{pmatrix}. \quad (1)$$

The seven independent elastic constants of $GdLiF_4$ structure versus pressure were calculated from stress-strain method using strain 0.002. The calculation parameters were the same as in section 2. On the figure 3 the elastic constants C_{11}, C_{12}, C_{13} and C_{33} show strong pressure dependence, in contrast to C_{16} and C_{44}. The value of C_{66} elastic constant decreases as a function of pressure.

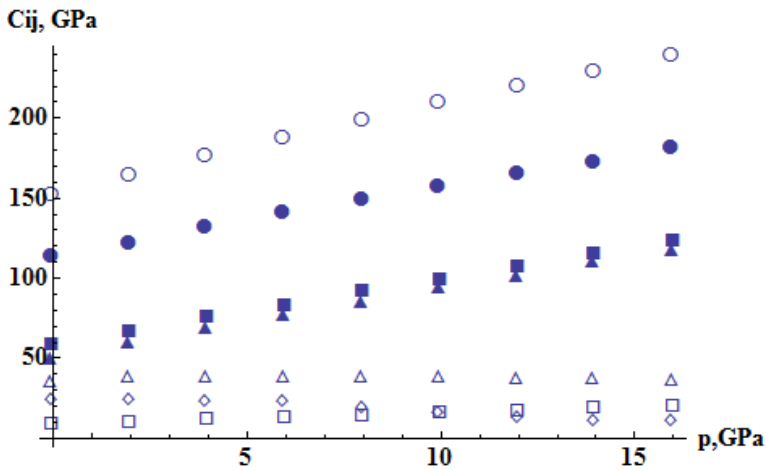

Figure 3. Evolution of elastic constants versus pressure (C_{11}-solid circle, C_{12}-solid triangle, C_{13}-solid square, C_{16}-empty square, C_{33}-empty circle, C_{44}-empty triangle, C_{66}-empty rhomb).

From the constants of elasticity the following modulus were calculated: shear module is equal to 34 GPaand Young's module is equal to 89 GPa.

By the fitting P-V curves with a Birch-Murnanghan equation of state,

$$P(V) = \frac{3B_0}{2}\left[(\frac{V_0}{V})^{\frac{7}{3}} - (\frac{V_0}{V})^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(B'_0 - 4)\left[(\frac{V_0}{V})^{\frac{2}{3}} - 1\right]\right\} \quad (2)$$

bulk modulus B_0,the first pressure derivative of the bulk modulus B'_0 and equilibrium volume V_0 were evaluated.The results are presented in the table 1.

Table 1. The comparison of the mechanical parameters.

Methods	**V_0, volume, $\mathring{A}^3$**	**B_0, Bulk modulus, GPa**	**B'_0, the first pressure derivative of the bulk modulus**
B-M	302.4	79	3.9
MT	302.4	80	-
B-M experiment[2]	302.9±0.3	76±4	5.01±1.03

A good agreement is observed between the bulk modules obtained by MT calculations, by Birch-Murnaghan (BM) approximation and experimental values (B-M approximation of experimental data).

It is well known that a Born condition of the stability of crystals demands the positive sign ofthe eigenvalues of the elastic constants matrix [8, 9]. MT calculations of $GdLiF_4$ structure give the negative eigenvalue above 10 GPa. It gives the evidence of the instability of $GdLiF_4$compound above this value of pressure as observed in the experiment [2] where decomposition of $GdLiF_4$ sample has been found at 13.1 GPa.

4. Conclusion

We obtained a good agreement of structural parameters (*A*, *C*, *C*/*A*, *V*) with experimental values. The pressure dependence of volume has been fitted with the Birch–Murnaghan equation of state to evaluate the equilibrium volume and the bulk modulus. Mechanical parameters (bulk modulus, B_0 and equilibrium volume, V_0) show a good agreement with the relevant values obtained in the experiment and directly calculated with using MT module. The seven independent elastic constants of $I4_1/a$ $GdLiF_4$ structure were evaluated versus pressure. Mechanical-thermal analysis of $GdLiF_4$ structure revealed the instability of this material above 10 GPa.

Acknowledgements

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