



Phase Transitions: A Multinational Journal

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpht20>

Pressure-induced ferroelastic phase transition in LuLiF_4 compound

A.V. Petrova^a, O.V. Nedopekin^a, B. Minisini^b & D.A. Tayurskii^{ac}

^a Institute of Physics, Kazan Federal University, Kazan, Russian Federation

^b Institut Supérieur des Matériaux et Mécaniques Avancés du Mans, Le Mans, France

^c Centre for Quantum Technologies, Kazan Federal University, Kazan, Russian Federation

Published online: 19 Feb 2015.



CrossMark

[Click for updates](#)

To cite this article: A.V. Petrova, O.V. Nedopekin, B. Minisini & D.A. Tayurskii (2015): Pressure-induced ferroelastic phase transition in LuLiF_4 compound, Phase Transitions: A Multinational Journal, DOI: [10.1080/01411594.2014.1000578](https://doi.org/10.1080/01411594.2014.1000578)

To link to this article: <http://dx.doi.org/10.1080/01411594.2014.1000578>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Pressure-induced ferroelastic phase transition in LuLiF_4 compound

A.V. Petrova^{a*}, O.V. Nedopekin^a, B. Minisini^b and D.A. Tayurskii^{a,c}

^a*Institute of Physics, Kazan Federal University, Kazan, Russian Federation;* ^b*Institut Supérieur des Matériaux et Mécaniques Avancés du Mans, Le Mans, France;* ^c*Centre for Quantum Technologies, Kazan Federal University, Kazan, Russian Federation*

(Received 9 September 2014; accepted 9 December 2014)

The behavior of LuLiF_4 scheelite ($I4_1/a$, $Z = 4$) under hydrostatic pressure was investigated by means of first principles calculations. The ferroelastic phase transition from the tetragonal structure of LuLiF_4 to the fergusonite structure ($C12/c1$, $Z = 4$) has been found at 10.5 GPa. It has been determined that this is the second-order phase transition.

Keywords: fluorides; high pressure; phase transitions; *ab initio* calculations

1. Introduction

The interest in fluorite rare-earth compounds (with the scheelite CaWO_4 structure) increases significantly due to their possible application in laser technologies and micro-electronics.[1,2] The intrinsic dipole moment materials invoke particular curiosity in a certain temperature range. One of these compounds (namely, LuLiF_4) has been recently investigated at high pressures by synchrotron angle-dispersive X-ray powder diffraction in a diamond anvil cell at room temperature.[3] A tricritical phase transition to the fergusonite crystal structure was found at 10.7 GPa, but the type of this phase transition remained unknown. The present article is devoted to searching for the phase transitions in LuLiF_4 at high pressures by the means of density functional theory (DFT) [4,5] and to the identification of its type.

2. Calculations

Two experimentally observed crystal structures of LuLiF_4 with the $I4_1/a$ ($a = b = 5.172588 \text{ \AA}$, $c = 10.586842 \text{ \AA}$, no. 88, $Z = 4$) and $C12/c1$ ($a = 7.32361 \text{ \AA}$, $b = 10.578649 \text{ \AA}$, $c = 5.165849 \text{ \AA}$, no. 15, $Z = 4$) symmetries and two possible crystal structures with the $P12/c1$ ($a = 5.077383 \text{ \AA}$, $b = 5.237221 \text{ \AA}$, $c = 5.237368 \text{ \AA}$, no. 13, $Z = 2$) and $P2_1/c$ LaTaO_4 -type ($a = 8.072336 \text{ \AA}$, $b = 5.393765 \text{ \AA}$, $c = 7.022196 \text{ \AA}$, no. 14, $Z = 4$) symmetries were investigated by means of *ab initio* calculations. The analogous crystal structure of YLiF_4 with the same symmetries has been studied by *ab initio* calculations, previously.[6] Also the phase transitions from the $I4_1/a$ to $C12/c1$ symmetry were investigated in YLiF_4 and YbLiF_4 compounds.[7,8] Grzechnik et al. [9] observed such a type of phase transition in YLiF_4 above 300 K, experimentally. In this work, VASP 5.2 (Vienna Ab-Initio Simulation Package)[10] software package, a part of the MedeA¹ modeling interface, was used to perform first principles DFT calculations. The geometry of

*Corresponding author. Email: Anastasiya.Petrova@kpfu.ru

structures was optimized in the pressure range from 0 to 20 GPa with a 2 GPa step until the maximum force dropped below 0.005 eV/\AA , whereas the self-consistent field energy convergence criterion was set at 10^{-6} eV .

All calculations were performed in ‘non-magnetical’ mode (i.e. two electrons in each state). The electronic degrees of freedom were described using the projector-augmented wave method [11] and basis of plane waves as implemented in VASP 5.2. The valence electrons of Lu were considered as ‘kept frozen in the core’. The exchange–correlation functional has been approximated by the gradient-corrected form proposed by Perdew–Burke–Ernzerhof [12]. The Dudarev approach [13] was applied within a simplified generalized gradient approximation (GGA)+U scheme. [12] The other calculation parameters were chosen to be the same as in Ref. [14].

3. Results

The analysis of the lattice parameters, unit cell volume, order parameter and bulk modulus under pressure has been performed in order to determine the type of the phase transition and to obtain the transition pressure. In Figure 1, the pressure dependencies of the lattice parameters (where a_m , b_m and c_m are the lattice parameters of monoclinic structure; a_0 , b_0 , c_0 are the respective values of the lattice parameters at ambient pressure) reflecting the transformation of the structure from the $I4_1/a$ to $C12/c1$ symmetry are shown. Since the $C12/c1$ symmetry group is in fact a subgroup of $I4_1/a$, the structural parameters of these symmetries coincide below 10.5 GPa. One can conclude from Figure 1 that the phase transition occurs at 10.5 GPa, which is in good agreement with the experimental data.[3]

In order to identify the type of the phase transition, the volumes of LuLiF_4 unit cell were calculated for two symmetries for pressure up to 20 GPa. Figure 2 demonstrates the difference of the cell volumes between two symmetries above 10.5 GPa. It is well known that the energy and volume of the system should be changed smoothly at the second-order phase transition,[15] which is accompanied by the changes of the system symmetry as is a

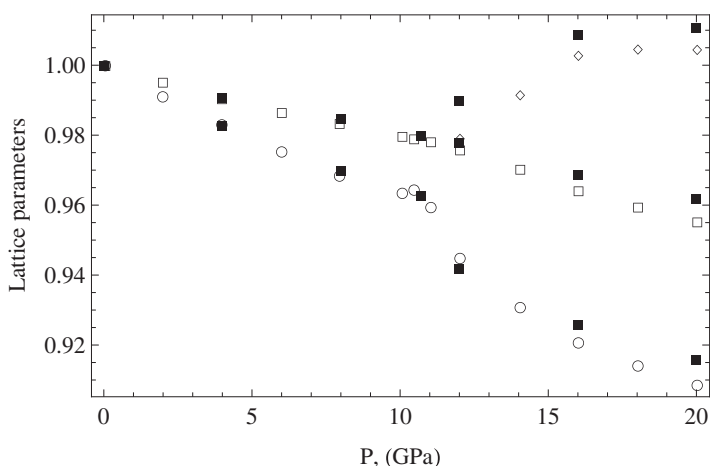


Figure 1. Pressure dependencies of the lattice parameters (LuLiF_4 structure, the $C12/c1$ symmetry) normalized to the corresponding value at ambient pressure: experimental data [3] – solid square; *ab initio* calculations: empty diamond – a_m/a_0 , empty square – b_m/b_0 , empty circle – c_m/c_0 .

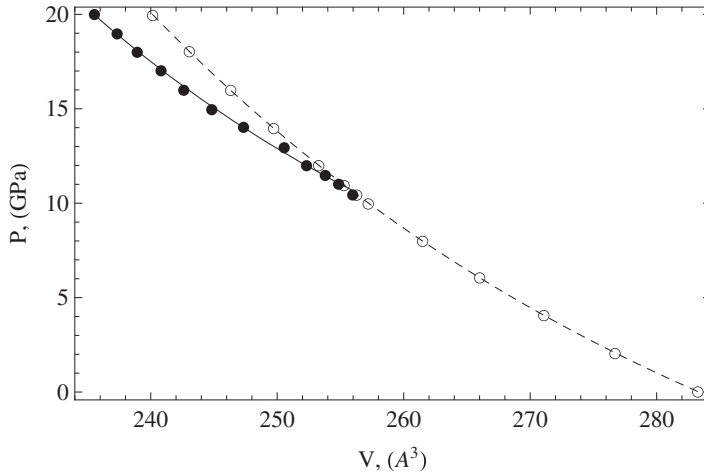


Figure 2. Pressure dependencies of the volumes of LuLiF₄ structure (empty circles: the unit-cell volume of the I₄/a LuLiF₄ structure versus the pressure; solid circles: the unit-cell volume of the C12/c1 LuLiF₄ structure versus the pressure, dashed and solid lines: Birch–Murnaghan approximation, respectively).

case of the present study. It follows from Figures 1 and 2 that the second-order phase transition occurs in the analyzed LuLiF₄ compound at high pressures.

The pressure dependence of the order parameter was plotted to find the critical pressure of the phase transition. The second rank strain tensor components have been selected as primary-order parameters.[3] The corresponding tensor function $\mathbf{e}_m = 1/\sqrt{2}(\mathbf{e}_{xx} - \mathbf{e}_{yy})$ [16] represents a basis function of the single dimensional irreducible representation B_g of the 4/m symmetry group, and it can be considered as the ferroelastic order parameter. The spontaneous strains \mathbf{e}_{xx} and \mathbf{e}_{yy} , contributing to the order parameter \mathbf{e}_m , are determined as follows: $\mathbf{e}_{xx} = (c_m - a_t)/a_t$ and $\mathbf{e}_{yy} = (a_m/\sqrt{2} - a_t)/a_t$ (where a_t is the lattice parameter of tetragonal structure, a_m and c_m are the lattice parameters of monoclinic structure). The order parameter starts changing smoothly from zero (I₄/a symmetry) to a non-zero (C12/c1 symmetry) value at the point 10.5 GPa (see Figure 3).

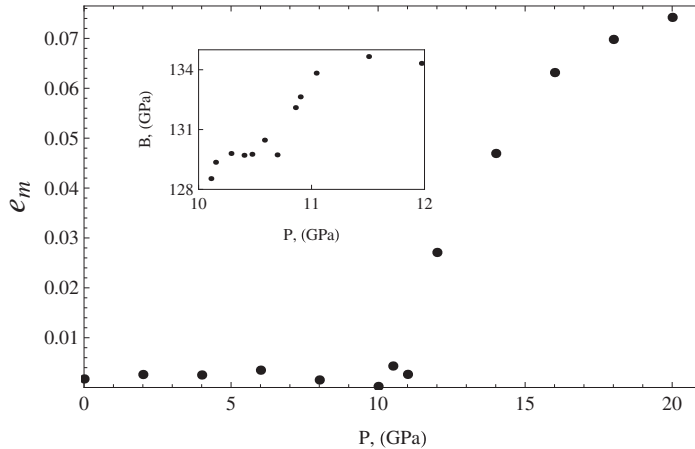


Figure 3. The order parameter of LuLiF₄ structure versus the pressure. Inset shows the pressure dependence of the bulk modulus of LuLiF₄ structure.

This type of the order parameter can be used due to the fact that the fergusonite structural model (space group C12/c1) was originated from the scheelite-type structure (space group I4₁/a [17]) because of supergroup–subgroup relationships.

The dependence of the bulk modulus B on pressure from 0 to 20 GPa was also investigated. This dependence has been plotted in the range of interest between 10 and 12 GPa to confirm the phase transition in this range. The change in the behavior has been observed from 10.5 to 11 GPa in Figure 3 (inset). The bulk modulus $B = 97$ GPa, volume $V = 282.45 \text{ \AA}^3$, and first pressure derivatives of the bulk modulus $B'_0 = 1.74$ for the C12/c1 symmetry were calculated by fitting the pressure–volume compression data with the Birch–Murnaghan equation of state.[18] The set of parameters for the I4₁/a symmetry at ambient pressure has been obtained previously: $B = 83$ GPa, $V = 283.4 \text{ \AA}^3$, $B'_0 = 4.5$. [14] It should be noted that the pressure derivatives of the bulk modulus for two symmetries of LuLiF₄ structure are different.

As mentioned above, the analogous YLiF₄ compound was studied by means of the DFT method, previously.[7] It was shown that YLiF₄ undergoes the phase transitions from the scheelite phase (I4₁/a, $Z = 4$) to the fergusonite-like phase (I₂/a, $Z = 4$) and to the LaTaO₄-like phase (P2₁/c, $Z = 4$). The scheelite-to-fergusonite transition is a second-order one as has been shown in many tungstates, molybdates and vanadates.[19,20] Also theoretical calculations have demonstrated the second-order nature of the phase transition in YLiF₄ and YVO₄ compounds.[6,21] To verify the phase transition to the P2₁/c and P12/c1 symmetries in LuLiF₄ compound, the pressure dependence of the enthalpy difference between the P2₁/c and P12/c1 phases with respect to the scheelite phase I4₁/a has been plotted in Figure 4.

The enthalpy of the C12/c1 phase becomes smaller than the enthalpy of the I4₁/a above 10.5 GPa, and the phase transition occurs. The enthalpy of structure with the P2₁/c symmetry is higher than the enthalpy of structure with the I4₁/a symmetry by 1.5 eV per elementary cell (LuLiF₄)₂. The enthalpy of the P12/c1 structure symmetry turned out to be higher than the enthalpy of structure with the I4₁/a symmetry by 0.9 eV per elementary cell (LuLiF₄)₂. Thus, LuLiF₄ structure with the I4₁/a symmetry is energetically most favorable at pressures below 10.5 GPa.

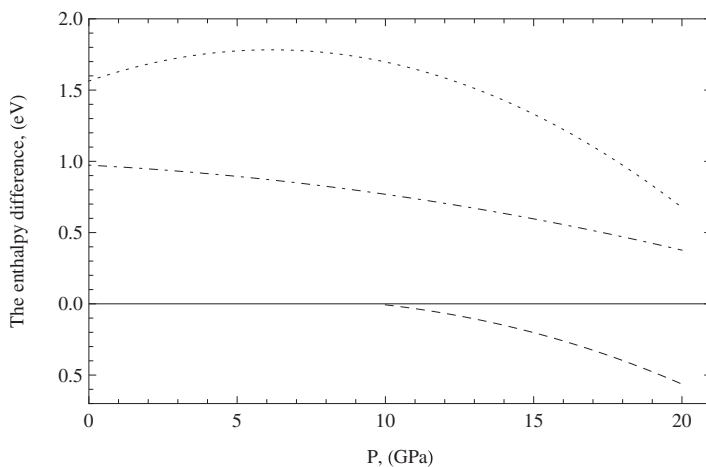


Figure 4. The enthalpy difference with respect to the scheelite phase I4₁/a for the C12/c1 (dashed line), P12/c1 (dash–dotted line), P2₁/c (dotted line) phases versus the pressure.

4. Conclusion

Thus, in this work the ferroelastic phase transition of the LuLiF_4 scheelite ($I4_1/a$, $Z = 4$) structure under pressure has been found at 10.5 GPa by means of DFT. The ferroelastic phase transition from the tetragonal structure to the fergusonite one ($C12/c1$, $Z = 4$) has been identified as the second-order transition from the pressure dependence of the structural parameters, order parameter and cell volume. The absence of the phase transitions to the $P2_1/c$ and $P12/c1$ structure symmetries has been shown.

Acknowledgements

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

Disclosure statement

No potential conflict of interest was reported by the authors.

Note

1. Materials Design, S.A.R.L.

References

- [1] Errandonea D, Manjón FJ, Somayazulu M, Häusermann D. Effects of pressure on the local atomic structure of CaWO_4 and YLiF_4 : mechanism of the scheelite-to-wolframite and scheelite-to-fergusonite transitions. *J Solid State Chem.* 2004;177(4–5):1087–1097.
- [2] Minisini B, Bonnaud P, Wang Q, Tsobnang F. DFT evaluation of thermomechanical properties of scheelite type MLiF_4 ($M = \text{La, Ce, Pr, Nd, Pm, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu}$). *Comput Mater Sci.* 2008;42(1):156–160.
- [3] Grzechnik A, Friese K, Dmitriev V, Weber HV, Gesland JY, Crichton W. Pressure-induced tricritical phase transition from the scheelite structure to the fergusonite structure in LiLuF_4 . *J Phys.* 2005;17(4):763.
- [4] Hohenberg P, Kohn W. Inhomogeneous electron gas. *Phys Rev.* 1964;136: B864–B871.
- [5] Kohn W, Sham LJ. Self-consistent equations including exchange and correlation effects. *Phys Rev.* 1965;140:A1133–A1138.
- [6] López-Solano J, Rodríguez-Hernández P, Muñoz A, Manjón FJ. Theoretical study of the scheelite-to-fergusonite phase transition in YLiF_4 under pressure. *J Phys Chem Solids.* 2006;67(9–10):2077–2082.
- [7] Minisini B, Hadj LE, Fomena ML, Garderen NV, Tsobnang F. A density functional study of the pressure induced phase transition in LiYF_4 . *J Phys.* 2006;18(8):2429.
- [8] Sen A, Chaplot S, Mittal R. Structural and dynamical consequences on various high-pressure phase transitions in laser host fluoroscheelites LiYF_4 and LiYbF_4 . *Curr Sci.* 2003;85(7):1045–1049.
- [9] Grzechnik A, Syassen K, Loa I, Hanfland M, Gesland JY. Scheelite to fergusonite phase transition in YLiF_4 at high pressures. *Phys Rev B.* 2002;65:104102.
- [10] Kresse G, Furthmüller J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys Rev B.* 1996;54:11169–11186.
- [11] Blöchl PE. Projector augmented-wave method. *Phys Rev B.* 1994;50:17953–17979.
- [12] Perdew JP, Burke K, Wang Y. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Phys Rev B.* 1996;54:16533–16539.
- [13] Dudarev SL, Botton GA, Savrasov SY, Humphreys CJ, Sutton AP. Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA+U study. *Phys Rev B.* 1998;57:1505–1509.

- [14] Petrova A, Minisini B, Nedopekin O, Tayurskii D. Ab-initio investigations of LuLiF_4 compound under pressure. *J Phys.* 2012;394(1):012021.
- [15] Landau L. The theory of phase transitions. *Nature.* 1936;138:840–841.
- [16] Tsunekawa S, Kamiyama T, Sasaki K, Asano H, Fukuda T. Precise structure analysis by neutron diffraction for RNbO_4 and distortion of NbO_4 tetrahedra. *Acta Crystallogr Section A.* 1993;49:595–600.
- [17] Garcia E, Ryan R. Structure of the laser host material LiYF_4 . *Acta Crystallogr Section C.* 1993;49:2053–2054.
- [18] Murnaghan F. The compressibility of media under extreme pressures. *Proceedings of the National Academy of Sciences of the United States of America.* 1944.
- [19] Errandonea D. Landau theory applied to phase transitions in calcium orthotungstate and isostructural compounds. *EPL.* 2007;77(5):56001.
- [20] Errandonea D, Manjón FJ. On the ferroelastic nature of the scheelite-to-fergusonite phase transition in orthotungstates and orthomolybdates. *Mater Res Bull.* 2009;44:807–811.
- [21] Manjón FJ, Rodríguez-Hernández P, Muñoz A, Romero AH, Errandonea D, Syassen K. Lattice dynamics of YVO_4 at high pressures. *Phys Rev B.* 2010;81:075202.