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Pressure-induced tricritical phase transition from the scheelite structure to the fergusonite structure in LiLuF_4

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Abstract

LiLuF_4 scheelite ($I4_1/a$, $Z = 4$) has been investigated at high pressures using synchrotron angle-dispersive x-ray powder diffraction in a diamond anvil cell at room temperature. At 10.7 GPa, it reversibly undergoes a tricritical phase transition to the fergusonite structure ($C12/c1$, $Z = 4$), a distorted modification of the scheelite type. No other phase transition occurs in this material up to 19.5 GPa, the highest pressure in this study. Such a high-pressure behaviour is compared with the pressure-induced transformations in LiYF_4 and LiGdF_4 , adding on to our knowledge of the structural systematics in LiMF_4 compounds.

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

1. Introduction

Pressure-induced phase transitions in the ABX_4 type compounds with the scheelite CaWO_4 structure have recently been the subject of several experimental and computational studies. The scheelite structure type ($I4_1/a$, $Z = 4$) is a superstructure of fluorite CaF_2 ($Fm\bar{3}m$, $Z = 4$) in which the oxygen atoms are in a distorted cubic arrangement while the Ca^{2+} and W^{6+} cations are fourfold and eightfold coordinated by fluorines, respectively. Continuous phase transformations to the fergusonite structure ($I2/a$, $Z = 4$) that is a distorted variant of

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the scheelite type have been observed in the oxides CaWO_4 [1], BaWO_4 [2], and CaMoO_4 [3] at high pressures.

Pressure-induced phase transitions in fluoride scheelites of the form LiMF_4 , where M is a trivalent cation, seem to be still debatable. LiYF_4 is known to transform to the fergusonite structure at about 10 GPa [4]. The same compound undergoes a transition to another polymorph at about 17 GPa, the crystal structure of which has yet not been determined. Molecular dynamics calculations of pressure-induced phase transitions in LiYF_4 and LiYbF_4 have predicted that their post-scheelite (post-fergusonite) polymorphs would be of the LaTaO_4 type ($P2_1/c$, $Z = 4$), with the Li^{1+} and Y^{3+} cations octahedrally and tenfold coordinated to the fluorine atoms, respectively [5]. Based on the total energy differences from electronic structure calculations assuming structural models isotypical to the BaWO_4 -II type ($P2_1/n$, $Z = 8$), LaTaO_4 type ($P2_1/c$, $Z = 4$), BaMnF_4 type ($Cmc2_1$, $Z = 4$), and NiWO_4 wolframite type ($P2/c$, $Z = 2$), Li *et al* have concluded that the post-fergusonite structure of LiYF_4 is of the wolframite type with all the cations octahedrally coordinated to fluorines [6]. However, wolframite is an ordered superstructure of $\alpha\text{-PbO}_2$ ($Pbcn$, $Z = 4$) and the transformation scheelite (fergusonite) \rightarrow wolframite postulated for the AMX_4 compounds [6, 7] is exactly opposed to the sequence observed in the AX_2 group of materials where the rutile type phases transform towards the fluorite related structures at high pressures, with the $\alpha\text{-PbO}_2$ -type structure being a possible intermediate [1, 8, 9].

Results of previous high-pressure high-temperature investigations on LiGdF_4 scheelite ($I4_1/a$, $Z = 4$) show that above 11 GPa it progressively decomposes into a solid solution series $\text{Li}_y\text{Gd}_{1-y}\text{F}_{3-2y}$ ($P6_3/mmc$, $Z = 2$) and LiF [10]. This demonstrates that apart from phase transformations into the BaWO_4 -II ($P2_1/n$, $Z = 8$), LaTaO_4 ($P2_1/c$, $Z = 4$), or BaMnF_4 ($Cmc2_1$, $Z = 4$) types, a decomposition of fluoride scheelites has to be additionally considered in order to establish a high-pressure high-temperature systematics of the AMX_4 type compounds.

The behaviour of scheelite-structured fluorides containing different rare earth metals as well as their structural relationship with LiYF_4 is of further interest. In this context, the goal of this study is to examine the high-pressure behaviour of LiLuF_4 to approximately 20 GPa using synchrotron angle-dispersive x-ray powder diffraction in a diamond anvil cell at high pressures and room temperature.

2. Experimental details

Angle-dispersive powder x-ray diffraction patterns were measured at room temperature and high pressure in a diamond anvil cell with a methanol:ethanol mixture as a pressure-transmitting medium on the Swiss–Norwegian Beamlines at the European Synchrotron Radiation Facility (BM1A, ESRF, Grenoble, France). Monochromatic radiation at 0.7100 Å was used for data collection on a MAR345 imaging plate. The stability of the wavelength over the time of the measurements was monitored by rechecking the distance between the detectors and samples (with the wavelength and calibrated sample d -spacings fixed). The images were integrated using the program FIT2D [11] to yield diagrams of intensity versus 2θ . The ruby luminescence method [12] was used for pressure measurements.

3. Results

X-ray powder diffraction patterns of LiLuF_4 at selected pressures are shown in figure 1. Upon compression up to about 10–11 GPa, all reflections can be indexed with the scheelite structure ($I4_1/a$, $Z = 4$). At higher pressure, a peak splitting and the appearance of new weak reflections

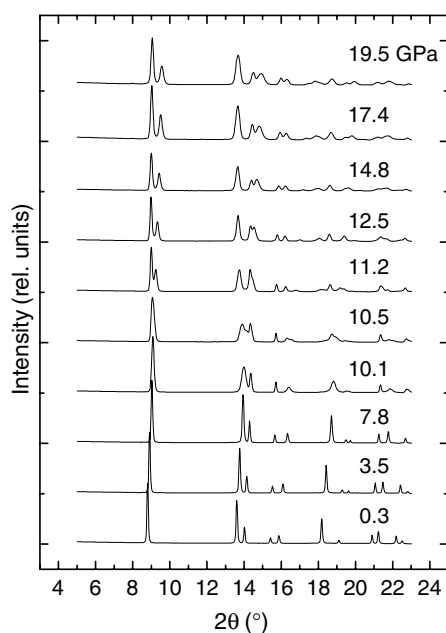


Figure 1. Selected x-ray powder patterns of LiLuF₄ upon compression ($\lambda = 0.7100 \text{ \AA}$).

imply a continuous phase transformation to a lower-symmetry structure of the fergusonite type ($C2/c$, $Z = 4$) that is a distorted variant of the scheelite type, previously observed in LiYF₄ [4], CaWO₄ [1], BaWO₄ [2], and CaMoO₄ [3]. No other phase transition is observed up to 19.5 GPa. The scheelite–fergusonite transformation in LiLuF₄ is fully reversible.

The fergusonite structural model (space group $C12/c1$) was derived from the scheelite type (space group $I4_1/a$, [13]) on the basis of supergroup–subgroup relationships. $C12/c1$ is a maximal subgroup of $I4_1/a$ with the index 2. The corresponding axis transformation is $a_m = -a_t - b_t$, $b_m = c_t$, $c_m = b_t$. The resulting relationship between the tetragonal and monoclinic unit cell parameters is $a_m \approx \sqrt{2}a_t$, $b_m \approx c_t$, $c_m \approx a_t$, with $\beta \approx 135^\circ$.

The model in the standard setting $C12/c1$ of space group no. 15 was optimized against the pattern collected at 11.9 GPa using the algorithm FOX [14] with parallel tempering, ‘smart’ temperature schedule, and exponential displacement schedule. Since the ratio of the number of observed Bragg peaks to the number of structural parameters was expected to be relatively low, the number of globally optimized parameters was reduced by introducing a rigid LiF₄ tetrahedron. Bonding and angular distortions of the LiF₄ tetrahedra were accounted for by relaxing the delta and sigma parameters in the program FOX [14]. Such a model was subsequently used for the structure refinement against the same pattern (figure 2) with the Rietveld method using the program GSAS [15]. The best fit was obtained at $R_{wp} = 17.00\%$, $R_p = 12.58\%$, and $R(F^2) = 13.78\%$ (the residuals R_{wp} and R_p have been calculated with the background eliminated; see the GSAS manual). The initial model contained a set of predefined distances between atoms, their corresponding standard deviations, and a weighting factor in order to add new ‘observables’ to the refinement. The starting minimal distances were 2.30(1) Å for F–F, 1.60(1) Å for Li–F, 3.40(1) Å for Li–Li, and 3.20(1) Å for Lu–Li. At the final stage of the refinement, only the Li–F bond constraint was used. Overall, the refined variables were: atomic positions, isotropic displacement parameters, lattice parameters, scale factor, zero shift, and Stephens profile function [16]. The obtained structural parameters are given in table 1. The Li–F bonds and next-nearest-neighbour Li–F distances are approximately 1.6 and

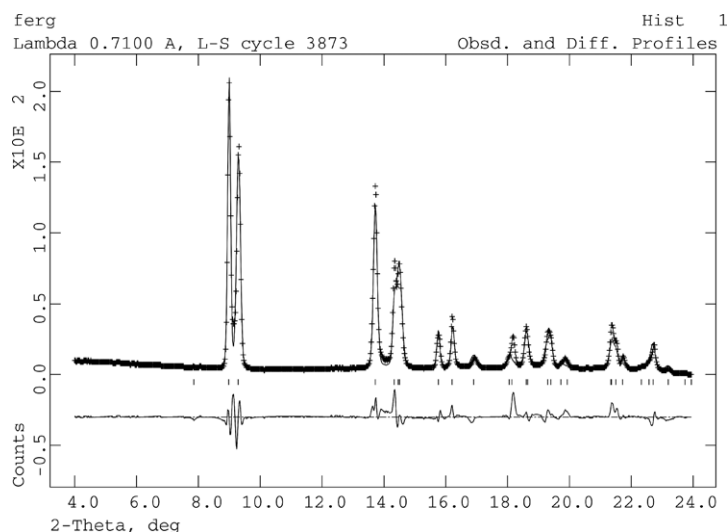


Figure 2. Observed, calculated, and difference x-ray powder patterns for fergusonite LiLuF_4 at 11.9 GPa ($\lambda = 0.7100 \text{ \AA}$)— $C12/c1$, $Z = 4$, $a = 7.2556(13) \text{ \AA}$, $b = 10.3510(17) \text{ \AA}$, $c = 4.8434(8) \text{ \AA}$, $\beta = 136.136(5)^\circ$. The vertical markers indicate Bragg reflections.

Table 1. Structural parameters for fergusonite LiLuF_4 at 11.9 GPa— $C12/c1$, $Z = 4$, $a = 7.2556(13) \text{ \AA}$, $b = 10.3510(17) \text{ \AA}$, $c = 4.8434(8) \text{ \AA}$, $\beta = 136.136(5)^\circ$. Estimated standard deviations are given in brackets.

Atom	Site	x	y	z	$U_i/U_e * 100$
Li	4e	0.0	0.0862(5)	0.25	33(13)
Lu	4e	0.0	0.6330(5)	0.25	14.89(25)
F1	8f	0.7779(5)	0.5435(11)	0.4181(18)	12.8(12)
F2	8f	0.9122(15)	0.8062(5)	0.4364(12)	5.3(9)

Selected bond distances (in \AA)					
Lu–F1	2.452(10)	2.452(10)	2.187(11)	2.187(11)	
Lu–F2	2.294(7)	2.294(7)	2.461(5)	2.461(5)	
Li–F1	1.5988(30)	1.5988(30)	2.632(8)	2.632(8)	
Li–F2	1.5995(33)	1.5995(33)			

2.6 \AA , respectively. Therefore, the highly deformed LiF_4^{3-} tetrahedra can still be considered to be isolated. All ions are significantly displaced from their ideal positions derived from the higher symmetrical scheelite model, implying the loss of the fourfold axis (figure 3).

Figure 4 shows the pressure dependences of the normalized lattice parameters, unit cell volumes, and axial ratios in LiLuF_4 and compares them with the corresponding values for LiYF_4 [4] and LiGdF_4 [10]. The lattice parameters and unit cell volume for LiLuF_4 scheelite at ambient pressure are $a = 5.1460(1) \text{ \AA}$, $c = 10.5886(2) \text{ \AA}$, and $V = 280.40(1) \text{ \AA}^3$. There is no discontinuity in the evolution of the unit cell volumes as well as of the c tetragonal and b monoclinic lattice parameters in LiLuF_4 . Of the three fluorides, LiLuF_4 scheelite is the least compressible along the a axis, and consequently its c/a axial ratio is the least pressure sensitive. The combined volume compression data for the scheelite and fergusonite polymorphs of LiLuF_4 up to 19.5 GPa could be fitted by a common Birch–Murnaghan equation of state to give the zero-pressure bulk modulus $B_0 = 85 \pm 3 \text{ GPa}$, the first pressure derivative of the bulk modulus $B' = 5.59 \pm 0.55$, and the unit cell volume of scheelite at ambient pressure

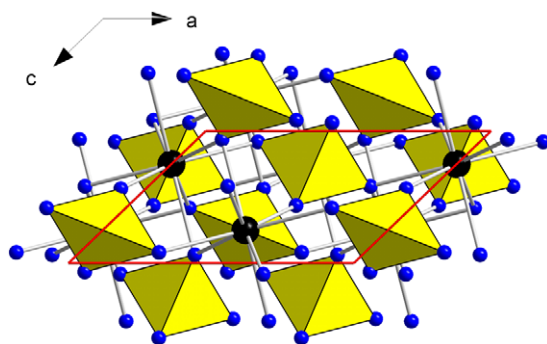


Figure 3. Crystal structure of LiLuF₄ fergusonite ($C12/c1$, $Z = 4$) in the (a, c) projection.

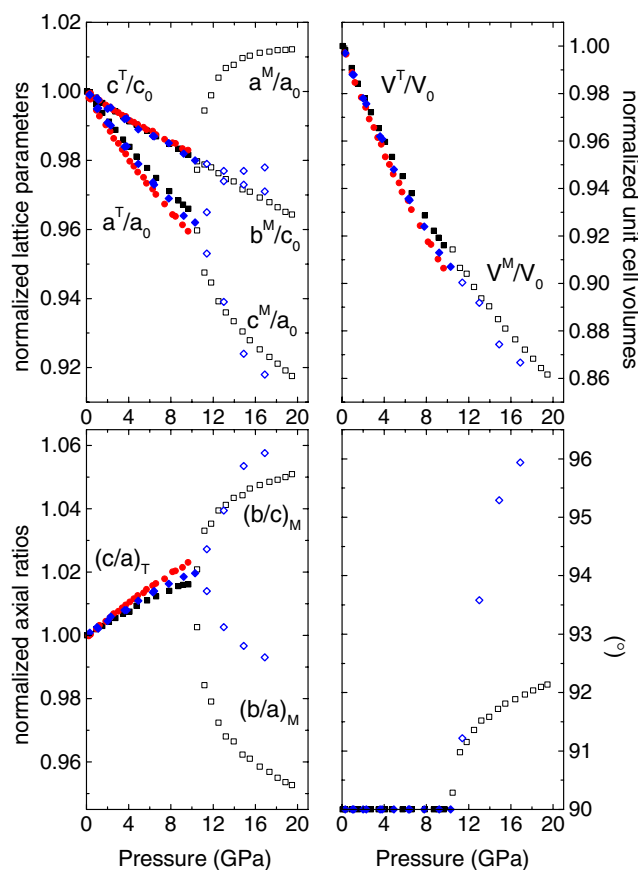


Figure 4. Pressure dependences of lattice parameters, unit cell volumes, and axial ratios in LiLuF₄ (black symbols) LiYF₄ (taken from [4], dark grey symbols) and LiGdF₄ (taken from [10], medium grey symbols) normalized to the respective values at ambient pressure. Full and open symbols stand for the scheelite ($I4_1/a$, $Z = 4$) and fergusonite (non-standard setting $I12/a1$, $Z = 4$) polymorphs, respectively.

$V_0 = 280.7 \pm 0.2 \text{ \AA}^3$ (table 2). Comparison of the equation-of-state parameters for all three fluorides shows that LiLuF₄ with the smallest unit cell volume of scheelite at ambient pressure has the largest bulk modulus.

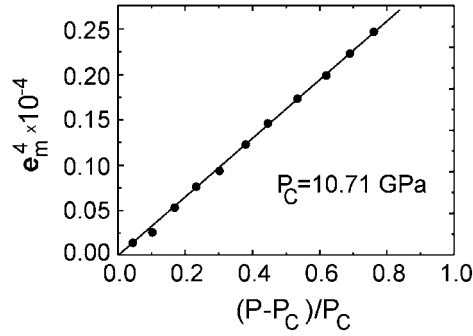


Figure 5. Pressure dependence of the fourth degree of the spontaneous strain in the monoclinic phase of LiLuF₄. The straight line is the best least-square fit.

Table 2. Equation-of-state parameters for LiLuF₄ determined in this study and compared with the parameters reported previously for LiYF₄ [4] and LiGdF₄ [10].

Material	Pressure range (GPa)	V_0 (\AA^3)	B_0 (GPa)	B'
LiLuF ₄	0–19.5	280.7 ± 0.2	85 ± 3	5.59 ± 0.55
LiYF ₄ [4]	0–17.4	285.1 ± 0.5	81 ± 4	4.97 ± 0.68
LiGdF ₄ [10]	0–11.0	302.9 ± 0.3	76 ± 4	5.01 ± 1.03

4. Discussion

In rare earth niobates and tantalates at atmospheric conditions, the temperature-induced ferroelastic scheelite \rightarrow fergusonite ($I4_1/a \rightarrow I2/a$, i.e., the non-standard setting of space group $C12/c1$) phase transition is associated with the anisotropic phonon softening of a transverse acoustic mode at the Brillouin zone centre [17]. As in lanthanide niobates and tantalates [17] and now in the pressure-induced fergusonite phase in LiYF₄ [4], it is debatable whether this transition is of the first or second order. It has been found experimentally that there is no volume change at the phase transition in LiYF₄ at about 10 GPa [4]. Electronic structure calculations indicate, however, that the scheelite–fergusonite transformation in this material takes place with a 0.5% volume collapse [6].

The scheelite \rightarrow fergusonite (equitranslational $4/m-2/m$) phase transition can be classified, in conventional terms [17], as a *proper ferroelastic* transformation. In such a transition, the second-rank strain tensor components play the role of a primary order parameter. The tensor function $\mathbf{e}_m = \frac{1}{\sqrt{2}}(\mathbf{e}_{xx} - \mathbf{e}_{yy})$ is a basis function of the relevant single-dimensional irreducible representation B_g of the $4/m$ symmetry group, and it transforms as the corresponding ferroelastic order parameter. Due to symmetry, only even-degree terms should be present in the free energy expansion: $\Delta G = A(P - P_C)\mathbf{e}_m^2 + B\mathbf{e}_m^4 + C\mathbf{e}_m^6$. It allows both first-order and second-order regimes for the transition between scheelite and fergusonite structures. However, our results indicate that a very particular transformation regime occurs in LiLuF₄. Figure 5 shows the plot of the fourth degree of the order parameter, \mathbf{e}_m^4 , calculated from the lattice parameters (figure 4) as a function of normalized pressure⁷. The linear character of the dependence reflects the *tricritical* nature of the corresponding phase transition, i.e., the

⁷ The spontaneous strains \mathbf{e}_{xx} and \mathbf{e}_{yy} , contributing to the order parameter \mathbf{e}_m , are determined as follows: $\mathbf{e}_{xx} = (c_m^{\text{exp}} - a_t^{\text{eos}})/a_t^{\text{eos}}$, $\mathbf{e}_{yy} = (a_m^{\text{exp}}/\sqrt{2} - a_t^{\text{eos}})/a_t^{\text{eos}}$. Here a_t^{eos} is the tetragonal lattice parameter extrapolated, with an equation of state, to the stability range of the monoclinic structure.

transition in LiLuF₄ passes through the tricritical point ($B = 0$) of the crossover from the second-order regime ($B > 0$) to the first-order one ($B < 0$) [18].

Our observation that in the pressure range 0–19.5 GPa the only phase transition in LiLuF₄ scheelite ($I4_1/a$, $Z = 4$) is the one to the fergusonite structure ($C12/c1$, $Z = 4$) significantly differs from the high-pressure behaviours of LiYF₄ [4] and LiGdF₄ [10] scheelites in the same pressure range. In LiYF₄, apart from the scheelite → fergusonite transformation at about 11 GPa, another structural transformation above 17 GPa to a yet undetermined polymorph has been detected [4]. LiGdF₄ behaves differently and decomposes above 11 GPa [10].

The results of this and previous studies [4, 10] show that the actual behaviour of scheelite-structured LiMF₄ fluorides is closely related to the radii of the M³⁺ cations. Of the three fluorides, LiLuF₄ has the smallest unit cell volume of scheelite at atmospheric pressure and has the largest bulk modulus. It remains to be seen whether such simple correlations between zero-pressure unit cell volumes in scheelites, bulk moduli, decomposition, and phase transitions to other crystalline polymorphs hold for the whole series of lithium lanthanide fluorides and LiYF₄. The competition between structural instabilities of the scheelite or fergusonite polymorphs and their decomposition needs to be further investigated.

5. Conclusions

The results of high-pressure investigations on LiLuF₄ scheelite ($I4_1/a$, $Z = 4$) using synchrotron angle-dispersive x-ray powder diffraction in a diamond anvil cell at room temperature show that above 10.7 GPa it reversibly transforms to the fergusonite structure ($C12/c1$, $Z = 4$), a distorted modification of the ambient pressure structure. No other phase transition is observed up to 19.5 GPa.

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