



	<b>Experiment title:</b> Fluoride scheelites at high pressures	<b>Experiment number:</b> HS-2179
<b>Beamline:</b> BM01A	<b>Date of experiment:</b> from: 09/04/2004 to: 13/04/2004	<b>Date of report:</b> 10/01/2005
<b>Shifts:</b> 12	<b>Local contact(s):</b> V. Dmitriev	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> A. Grzechnik*, Univ. País Vasco K. Friese*, Univ. País Vasco H.-P. Weber*, SNBL V. Dmitriev*, SNBL		

**Report:**

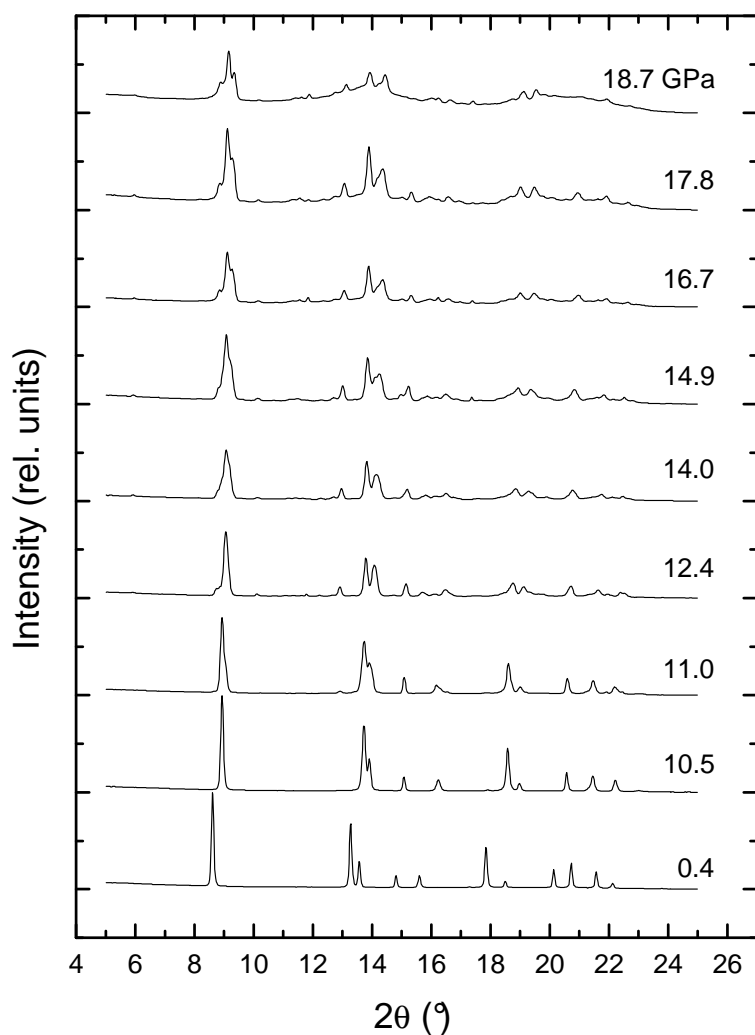
The results of this project were published in two publications in J. Phys.: Condens. Matter.

**Andrzej Grzechnik, Wilson A. Crichton, Pierre Bouvier, Vladimir Dmitriev, Hans-Peter Weber, and Jean-Yves Gesland - Decomposition of LiGdF<sub>4</sub> scheelite at high pressures - J. Phys.: Condensed Matter 16, 7779 (2004)**

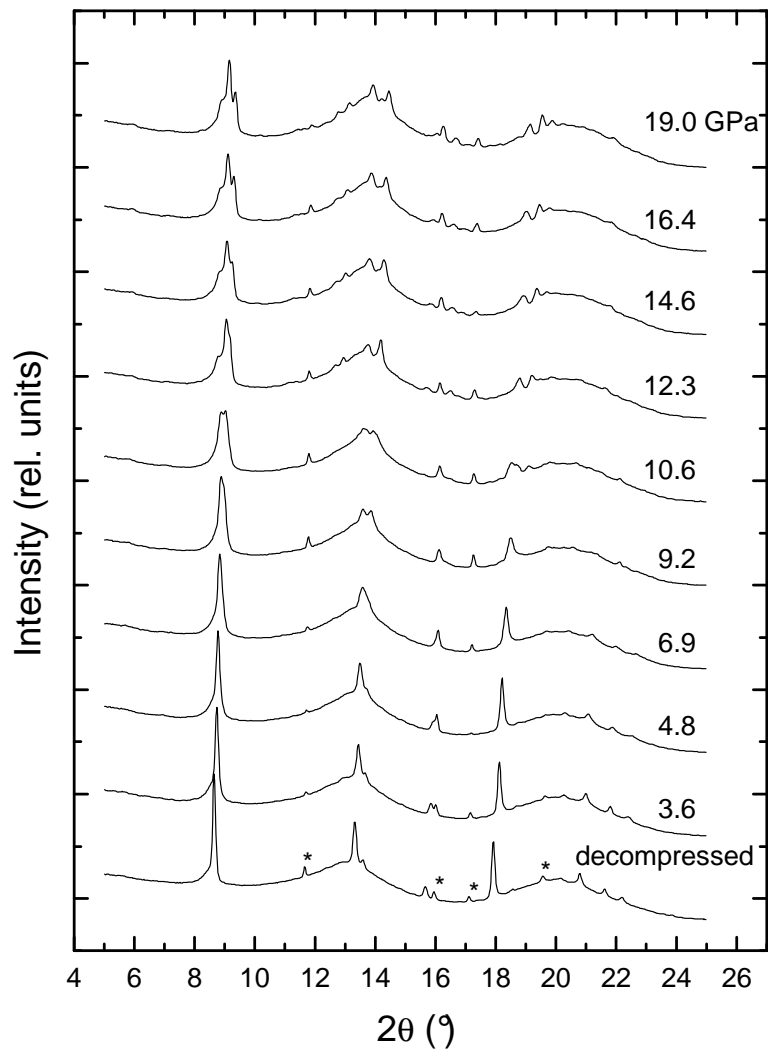
Abstract

High-pressure behavior of LiGdF<sub>4</sub> scheelite ( $I4_1/a$ ,  $Z = 4$ ) was studied by measuring its angle-dispersive x-ray powder diffraction patterns as a function of pressure and temperature in a diamond anvil cell and a large-volume Paris-Edinburgh cell using a synchrotron radiation source. Upon compression to about 11 GPa at room temperature, the stable structure is of the scheelite type. At higher pressures and  $T = 298$  K, new reflections occur that can not be explained with the fergusonite structural model previously observed in LiYF<sub>4</sub>. Associated is the growth of an amorphous component.

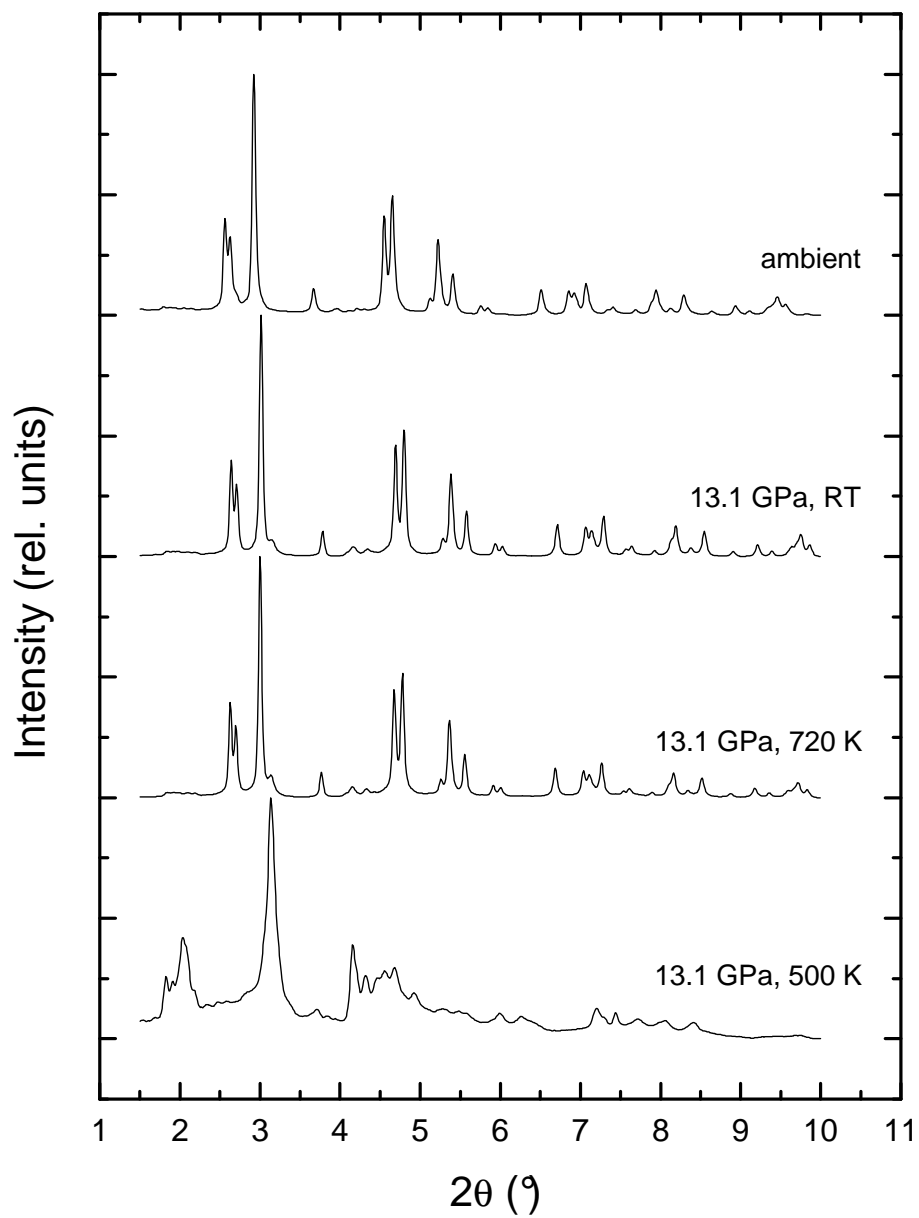
All the transformations are largely irreversible upon decompression. Annealing of the sample at 13.1 GPa led to a nucleation of a solid solution series  $\text{Li}_y\text{Gd}_{1-y}\text{F}_{3-2y}$  ( $P6_3/mmc$ ,  $Z = 2$ ) and traces of  $\text{LiF}$ . The new material  $\text{Li}_y\text{Gd}_{1-y}\text{F}_{3-2y}$  ( $P6_3/mmc$ ,  $Z = 2$ ) was recovered to ambient conditions but back-transformed to a  $\text{YF}_3$ -type phase ( $Pnma$ ,  $Z = 4$ ) after regrinding at room temperature in several hours. These observations are discussed in relation to the high-pressure high-temperature systematics of the  $\text{AMX}_4$  type compounds.



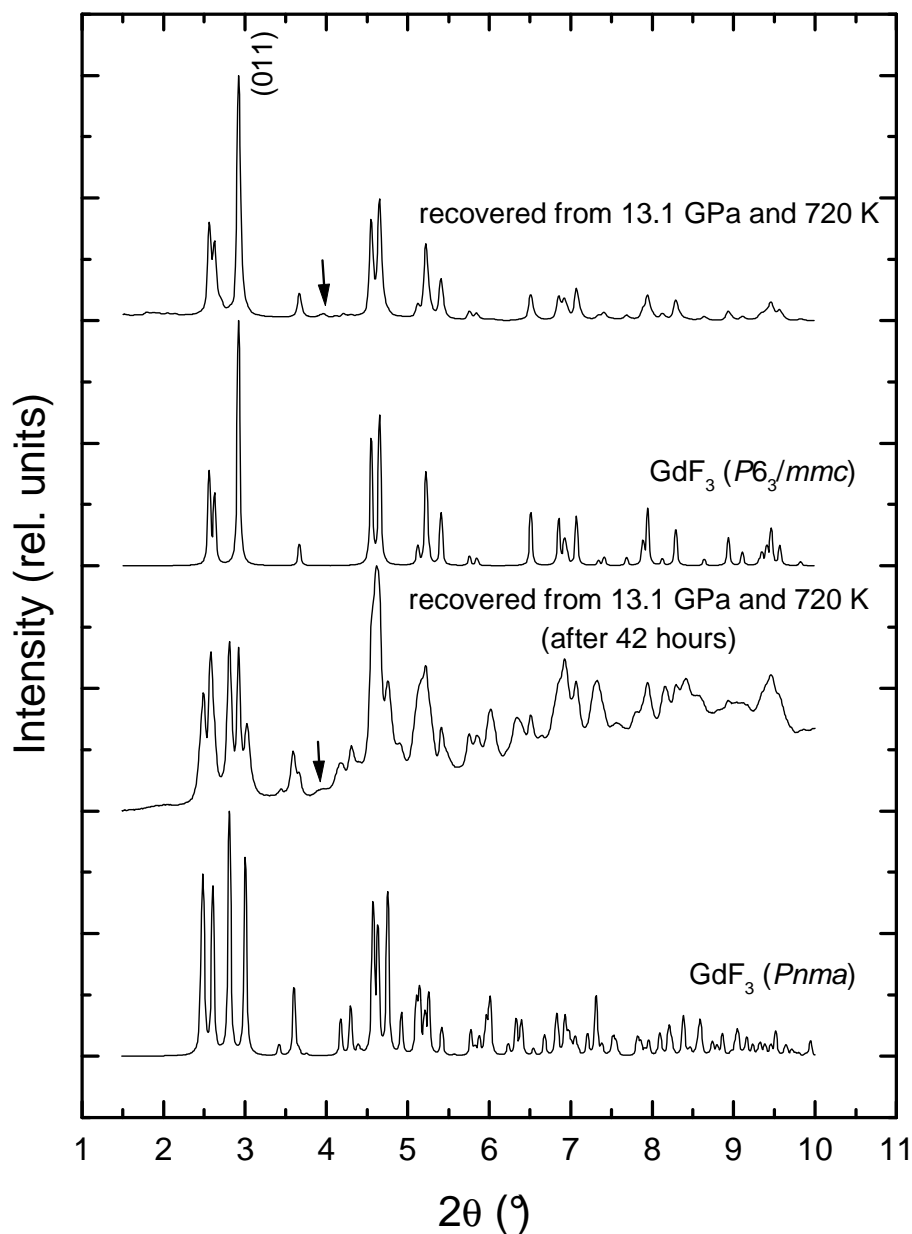
**Figure 1** Selected x-ray powder patterns collected in a diamond anvil cell at different pressures upon compression and room temperature,  $\lambda = 0.7100 \text{ \AA}$  (Swiss Norwegian Beamlines, ESRF).



**Figure 2** Selected x-ray powder patterns collected in a diamond anvil cell at different pressures upon decompression and room temperature,  $\lambda = 0.7100 \text{ \AA}$  (Swiss Norwegian Beamlines, ESRF). Stars indicate reflections due to Cr-doped  $\text{Al}_2\text{O}_3$  (ruby) used as a pressure calibrant.



**Figure 3** Selected x-ray powder patterns collected in a large-volume Paris-Edinburgh cell at different pressures and temperatures,  $\lambda = 0.15816 \text{ \AA}$  (ID30 Beamline, ESRF).

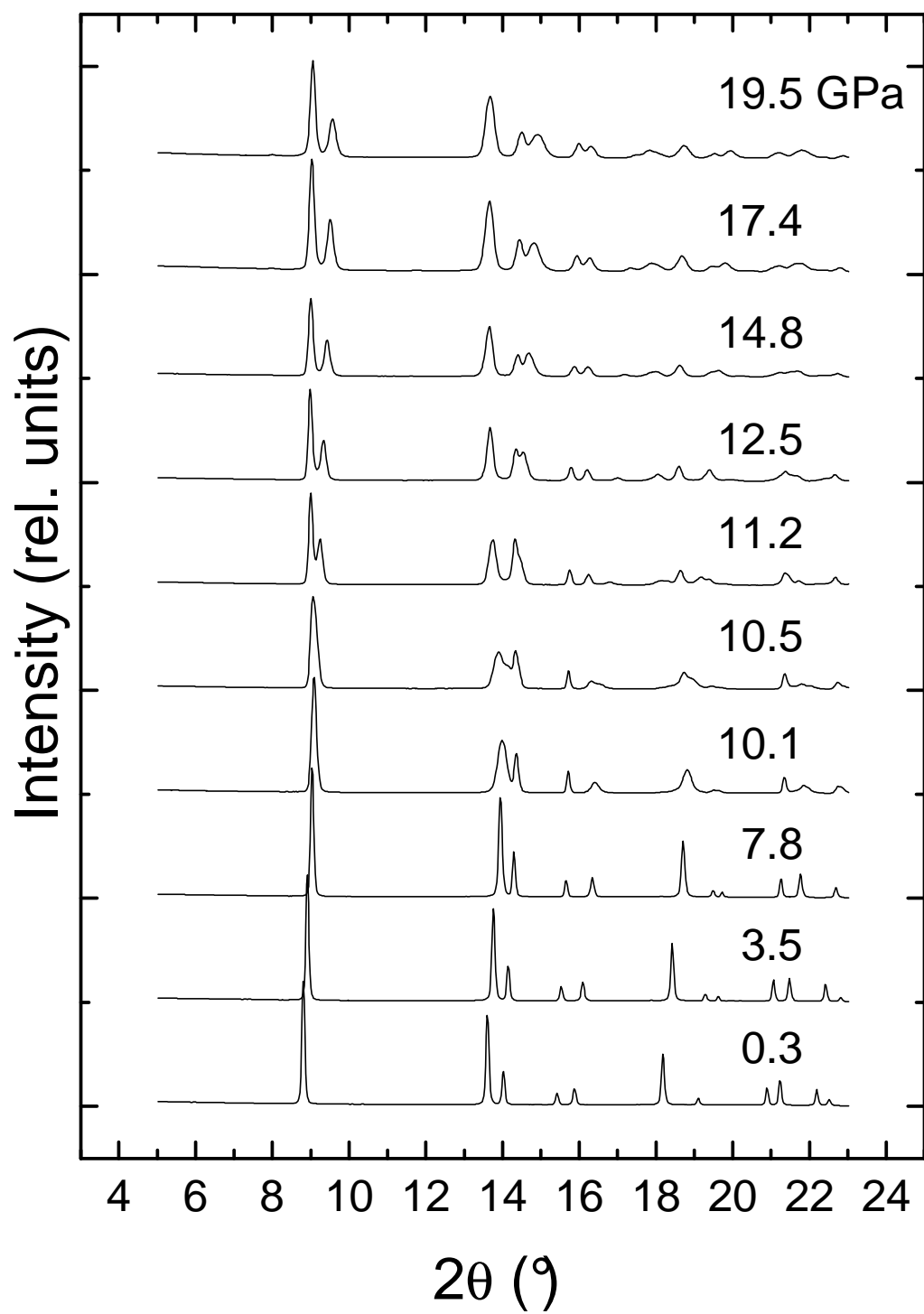


**Figure 4** Comparison of measured patterns for the recovered sample immediately after the experiment and after 42 hours (ID30 Beamline, ESRF) with calculated patterns for pure GdF<sub>3</sub> in the tysonite (*P6<sub>3</sub>/mmc*,  $Z = 2$ ,  $a = 3.985(1)$  Å,  $c = 7.081(2)$  Å) and  $\square$ -YF<sub>3</sub> (*Pnma*,  $Z = 4$ ,  $a = 6.696(2)$  Å,  $b = 6.962(2)$  Å,  $c = 4.342(1)$  Å) structures,  $\lambda = 0.15816$  Å. The (011) reflection in the tysonite type is marked. The arrows indicate the (111) reflection due to LiF.

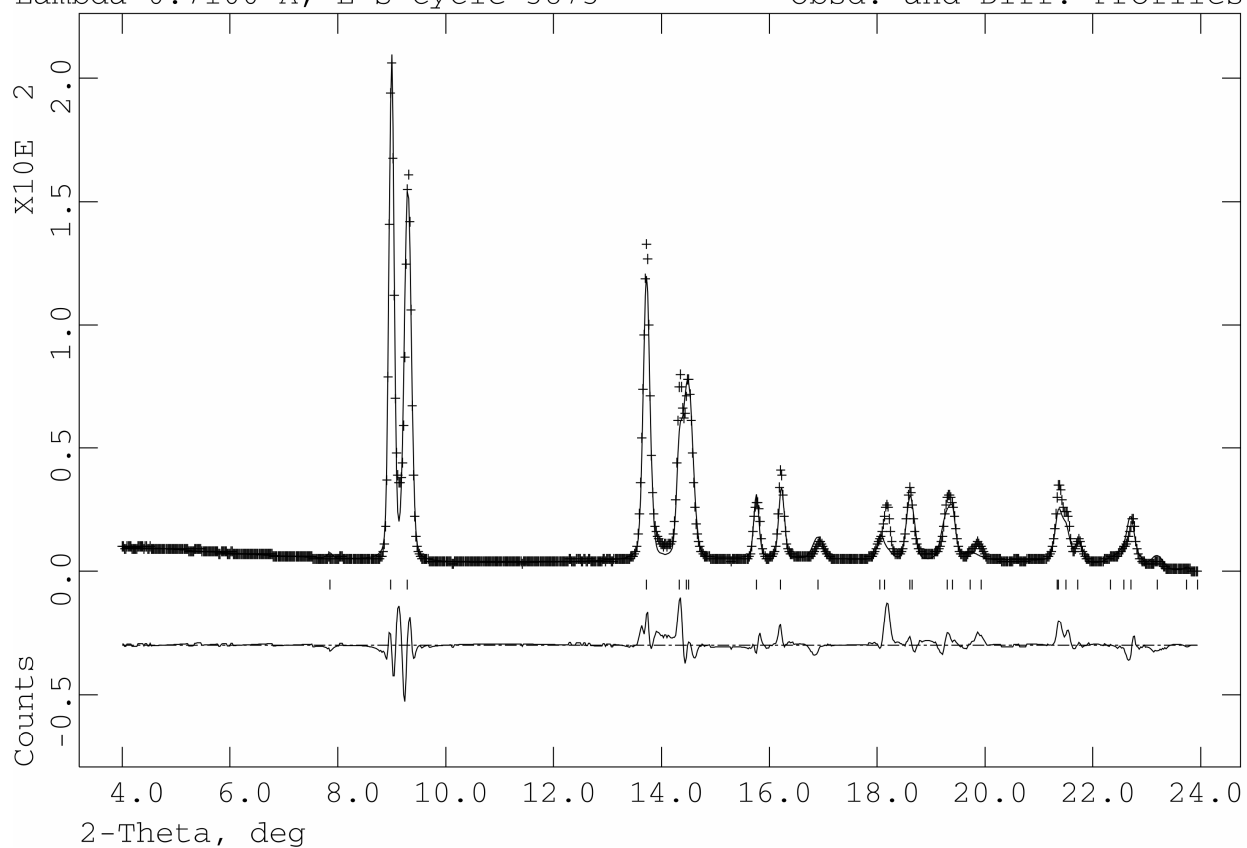
**Andrzej Grzechnik, Karen Friese, Vladimir Dmitriev, Hans-Peter Weber, Jean-Yves Gesland, and Wilson A. Crichton - Pressure-induced tricritical phase transition from the scheelite to the fergusonite structures in LiLuF<sub>4</sub> - J. Phys.: Condens. Matter, in press (2005)**

*Abstract*

LiLuF<sub>4</sub> 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 behavior is compared with the pressure-induced transformations in LiYF<sub>4</sub> and LiGdF<sub>4</sub>, adding on to our knowledge of the structural systematics in LiMF<sub>4</sub> compounds.

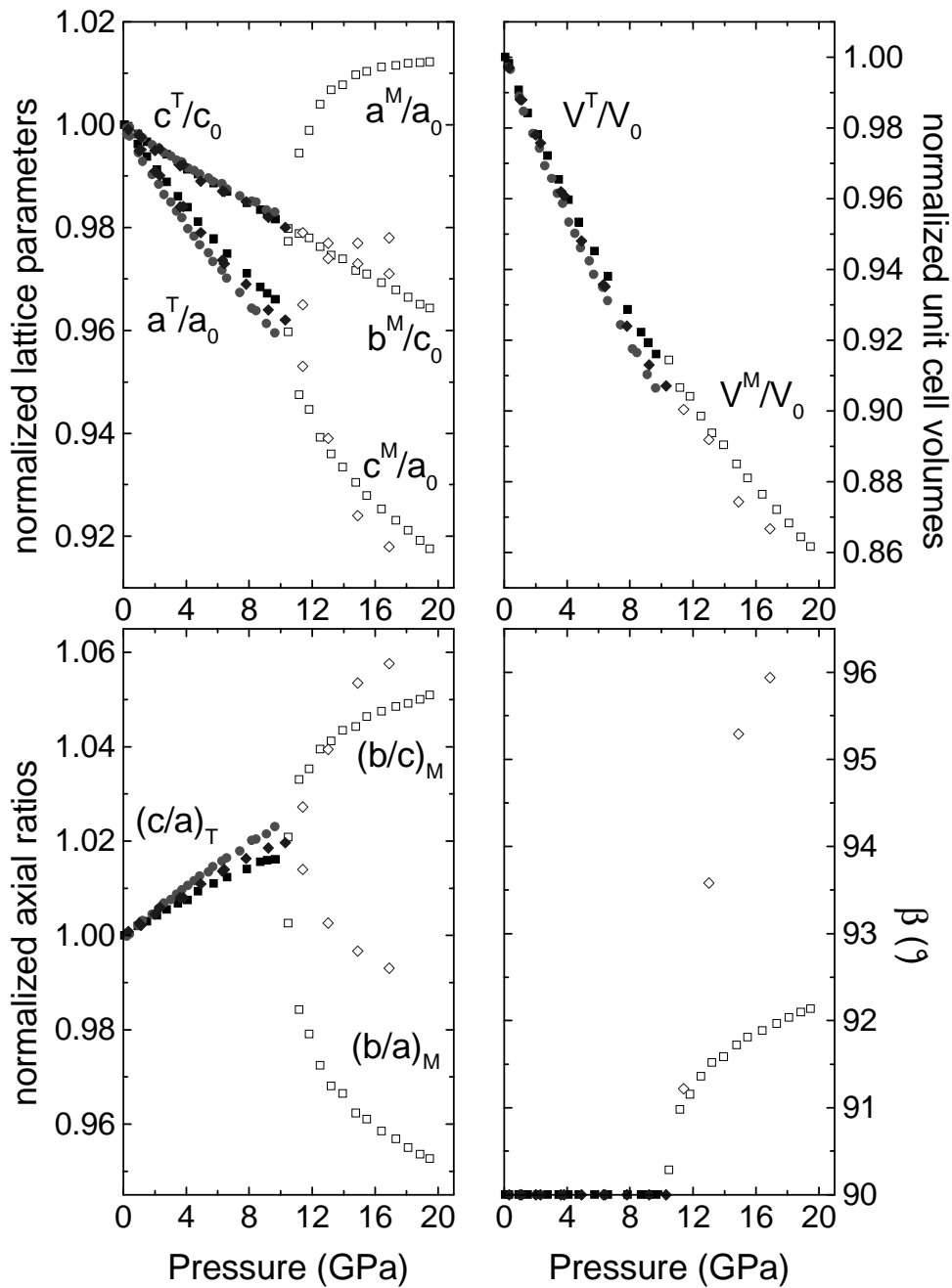


**Figure 1** Selected x-ray powder patterns of LiLuF<sub>4</sub> upon compression ( $\lambda = 0.7100 \text{ \AA}$ )

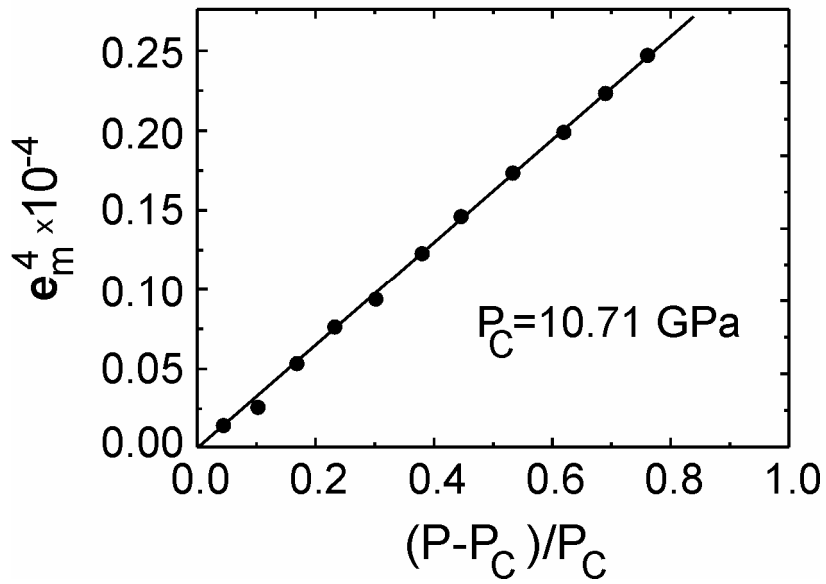


**Figure 2** Observed, calculated, and difference x-ray powder patterns for fergusonite LiLuF<sub>4</sub> at 11.9 GPa ( $\lambda = 0.7100 \text{ \AA}$ ) -  $C12/c1$ ,  $Z = 4$ ,  $a = 7.2556(13) \text{ \AA}$ ,  $b = 10.3510(17) \text{ \AA}$ ,  $c = 4.8434(8) \text{ \AA}$ ,  $\beta = 136.136(5)^\circ$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





**Figure 3** Pressure dependencies of lattice parameters, unit cell volumes, and axial ratios in LiLuF<sub>4</sub> (black symbols) LiYF<sub>4</sub> (blue symbols) and LiGdF<sub>4</sub> (red 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.



**Figure 5** Pressure dependence of the fourth degree of the spontaneous strain in the monoclinic phase of  $\text{LiLuF}_4$ . The straight line is the best least-square fit.