ESRF	**Experiment title:** Fluoride laser hosts at high pressures and high temperatures: Li_2ZrF_6	**Experiment number**: HS-2179
Beamline: BM01A	**Date of experiment**: from: 17/09/2003 to: 21/09/2003	**Date of report**: 30/05/2004
Shifts: 18	**Local contact(s)**: V. Dmitriev	*Received at ESRF:*

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Report:

Dilithium zirconium hexafluoride, Li_2ZrF_6 ($P\bar{3}1m$, Z = 1), is studied at high pressures using synchrotron angle-dispersive x-ray powder diffraction in a diamond anvil cell at room temperature. At atmospheric conditions, it has a structure with all the cations octahedrally coordinated to fluorine atoms. There occurs a fully reversible first-order phase transition above 10 GPa to a new polymorph (C2/c, Z = 4), in which the coordination polyhedron of the Zr atoms is a distorted square antiprism, while the Li atoms are in the octahedral coordination. The LiF_6 octahedra form layers parallel to (100) that are connected by zig-zag chains of the edge-sharing Zr polyhedra running in the [001] direction. The relative change in volumes per one formula unit for both polymorphs is 6% at 11.8 GPa.

Table Structural parameters for Li_2ZrF_6 (C2/c, Z = 4) at 14.8 GPa – a = 9.651(6) Å, b = 7.533(8) Å, c = 4.988(3) Å, β = 114.94(4)°, V = 328.8(4) $Å^3$. Estimated standard deviations are given in parenthesis. The symbols (2x) indicate the multiplicity.

Atom	Site	x	y	z
Li	8f	0.255(7)	0.536(9)	0.576(15)
Zr	4e	0.0	0.315(1)	0.25
F1	8f	0.121(3)	0.233(3)	0.060(6)
F2	8f	0.395(4)	0.041(3)	0.350(6)
F3	8f	0.112(2)	0.101(3)	0.480(6)

Selected distances (Å)

Li_F1	2.16(6)		Li_F1	2.65(7)
Li_F1	2.19(6)		Li_F2	2.01(6)
Li_F2	1.74(6)		Li_F3	2.09(7)
Li_F3	1.76(6)			
Zr_F1	1.89(2)	(2x)		
Zr_F2	2.15(2)	(2x)		
Zr_F2	2.12(2)	(2x)		
Zr_F3	2.02(2)	(2x)		

Figure Captions

Figure 1 Selected x-ray powder patterns of Li_2ZrF_6 at different conditions with argon as a pressure transmitting medium (λ = 0.71998 Å). Reflections due to argon are marked with stars.

Figure 2 Pressure dependence of unit-cell parameters and volumes in Li_2ZrF_6. Open and full symbols stand for the $P\bar{3}1m$ (Z = 1) and C2/c (Z = 4) polymorphs, respectively. The unit cell volumes of the monoclinic phase are divided by a factor of four. The relative volume change at 11.8 GPa is 6%.

Figure 3 Observed, calculated, and difference x-ray powder patterns for Li_2ZrF_6 (C2/c, Z = 4) at 14.8 GPa as obtained after the final Rietveld refinement (λ = 0.71998 Å). Vertical markers indicate the positions of Bragg reflections. The 2θ regions 15.8-16.9° and 18.35-19.06°, in which two reflections due to argon are observed, were excluded from the Rietveld refinement. Broad features at about 2θ = 8.9º and 2θ = 13.6º are the traces of the low-pressure phase ($P\bar{3}1m$, Z = 1), i.e, the (001) and (101) reflections, respectively.

Figure 4 Crystal structure of Li_2ZrF_6 (C2/c, Z = 4) at 14.8 GPa.

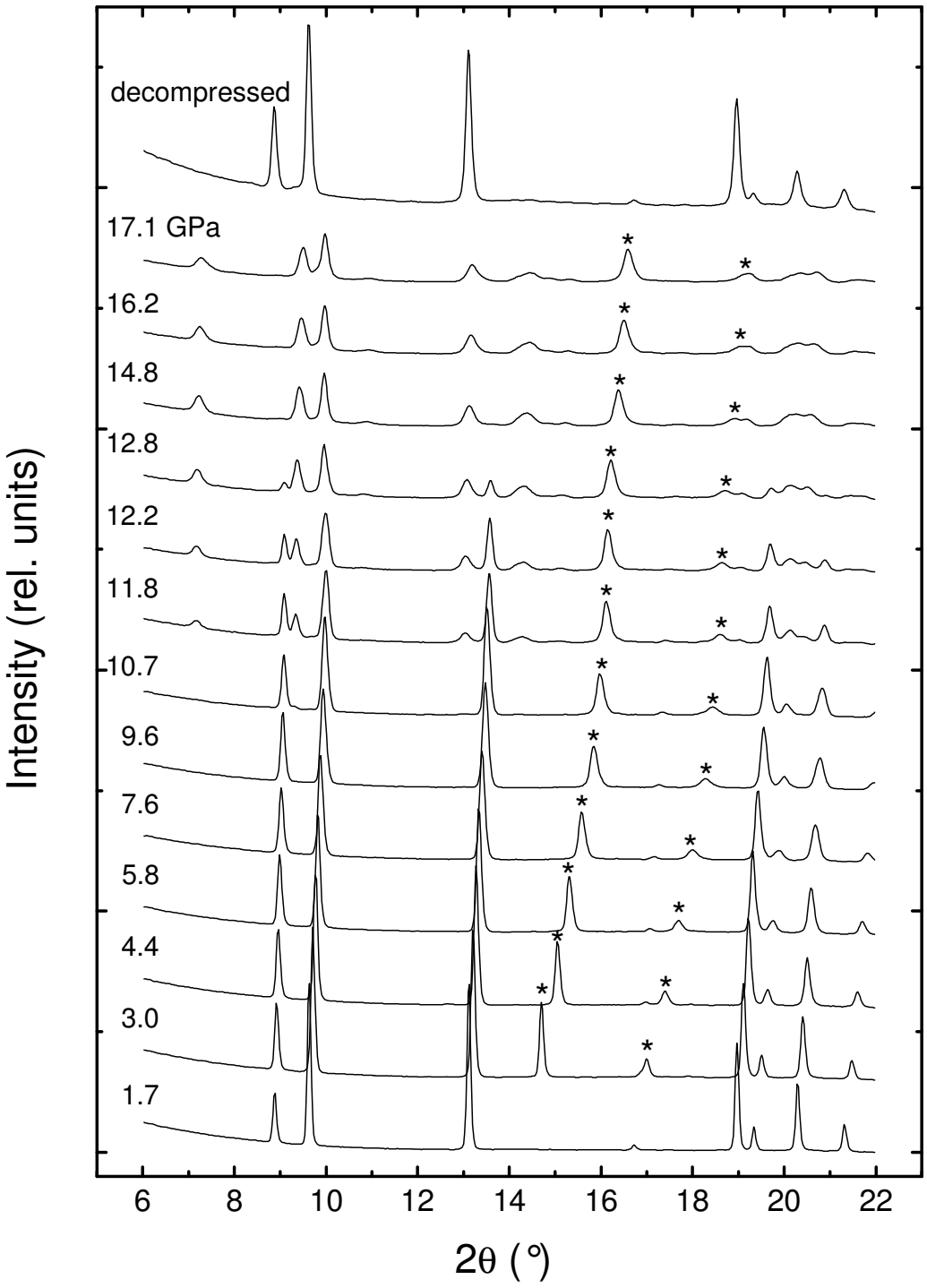
decompressed
17.1 GPa
16.2
14.8
12.8
12.2
11.8
10.7
9.6
7.6
5.8
4.4
3.0
1.7
Intensity (rel. units)
6
8
10
12
14
16
18
20
22
2θ (°)

Figure 1.

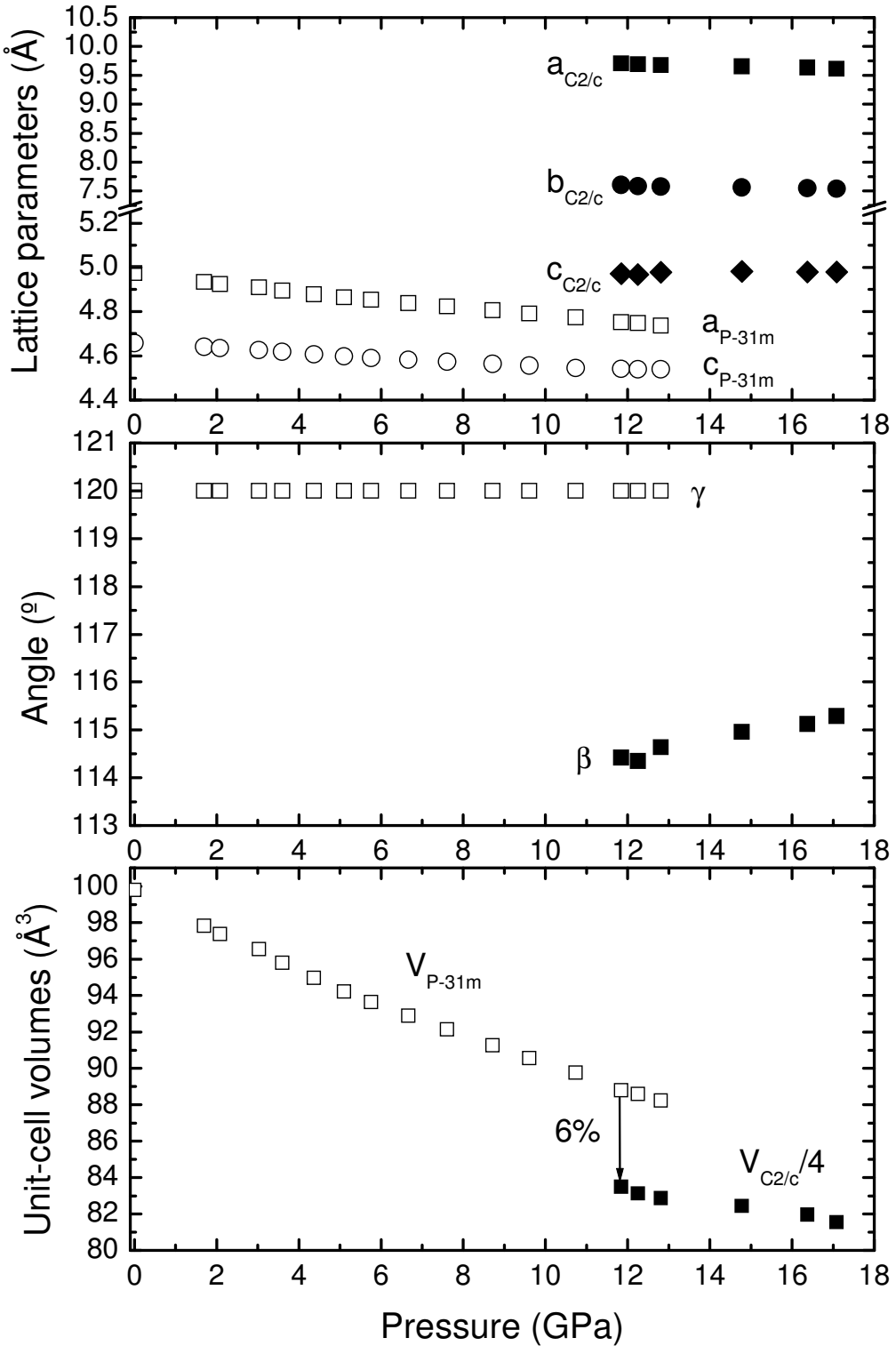
Lattice parameters (Å)
$a_{C2/c}$
$b_{C2/c}$
$c_{C2/c}$
a_{P-31m}
c_{P-31m}
Angle (º)
γ
β
Unit-cell volumes (Å^3)
V_{P-31m}
6%
$V_{C2/c}/4$
Pressure (GPa)

Figure 2.

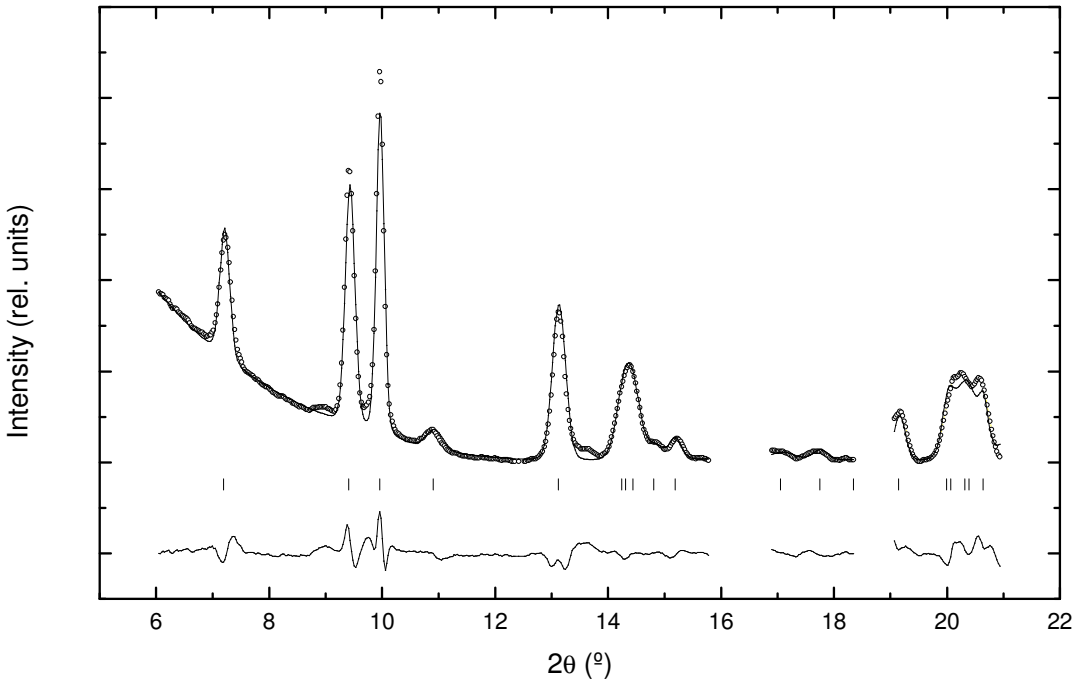

Figure 3.

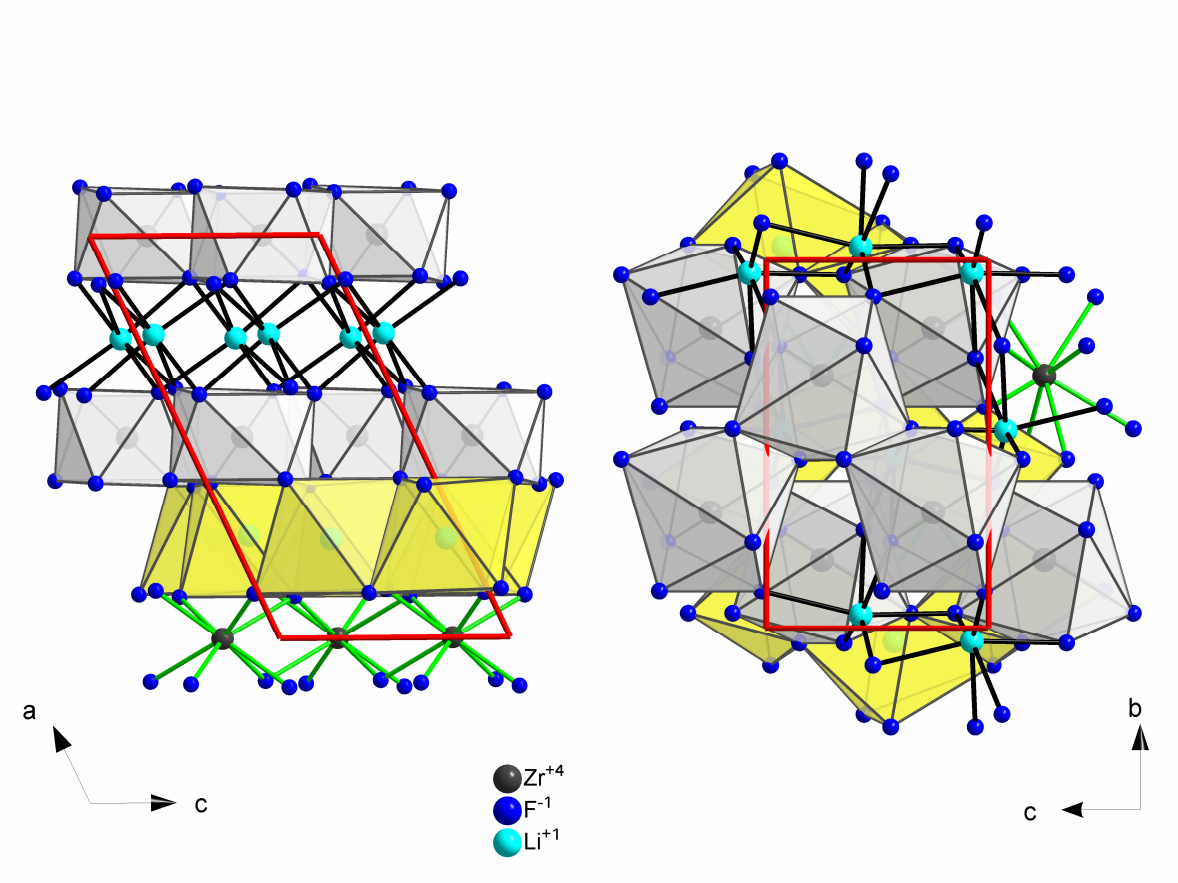

Figure 4.