



Beamline: BM01A	Experiment title: Fluoride laser hosts at high pressures and high temperatures	Experiment number: HS-2179
	Date of experiment: from: 17/09/2003 to: 21/09/2003	Date of report: 03/08/2004
	Shifts: 12	Local contact(s): V. Dmitriev
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Report:

The *colquiriite* family of fluoride compounds $\text{LiMM}'\text{F}_6$ ($\text{M} = \text{Ca}$ or Sr ; $\text{M}' = \text{Al}$, Ga , or Cr) is considered to be the most promising class of materials for optical applications like laser hosts and scintillating materials [1-9]. The crystal structure of LiSrAlF_6 -I ($P\bar{3}1c$, $Z = 2$) is an ordered derivative of the Li_2ZrF_6 type ($P\bar{3}1m$, $Z = 1$) [10], with each cation occupying a deformed octahedral site within the hexagonal-closest-packed arrangement of fluorine atoms. The polyhedral distortions in $\text{LiMM}'\text{F}_6$ have been correlated with the sizes of the M and M' cations [8,10,11]. For the M site occupied by luminescent dopants, the distortion, larger for the Sr compounds, is associated with the relative rotations of the two opposite trigonal F faces. As a consequence, the strontium-containing materials provide larger optical absorption coefficients determined by the strengths of static and dynamic distortions of the crystal field [11].

Information on the high-pressure behavior of the *colquiriite* compounds $\text{LiMM}'\text{F}_6$ ($\text{M} = \text{Ca}$ or Sr ; $\text{M}' = \text{Al}$, Ga , or Cr) is not available in the literature. At high pressures and high temperatures [12,13], Li_2ZrF_6 transforms into a polymorph with the Li_2TbF_6 structure ($P2_1/c$, $Z = 4$) [14], in which the zirconium atoms have a bicapped trigonal prismatic coordination, forming edge-sharing chains along the a axis. The Li^{1+} cations are in two types of coordination: octahedra and square pyramids. This

structure could be considered a distorted variant of the γ - Na_2UF_6 ordered *fluorite* (*Immm*, $Z = 2$), in which all the cations are surrounded by fluorines in a cube coordination [14]. The understanding of pressure-induced phase transitions, structures, and optical properties of the colquiriite materials could be improved by further investigations of the transformations involving changes in coordination spheres of the cations. Phonon energies, influencing luminescence efficiencies, are structure dependent and could be lowered by pressure-induced phase transitions to the polymorphs with increased coordination numbers around luminescent sites.

In the course of our work on high-pressure high-temperature behaviour of the the *colquiriite* compounds $\text{LiMM}'\text{F}_6$ ($M = \text{Ca}$ or Sr ; $M' = \text{Al}$ or Ga), we have found that LiSrAlF_6 and LiCaAlF_6 undergo a series of reversible pressure-induced structural transformations at room temperature. We thus investigated the crystal structures of new polymorphs of LiSrAlF_6 and of LiCaAlF_6 *in situ* in a diamond anvil cell with synchrotron angle-dispersive x-ray powder diffraction.

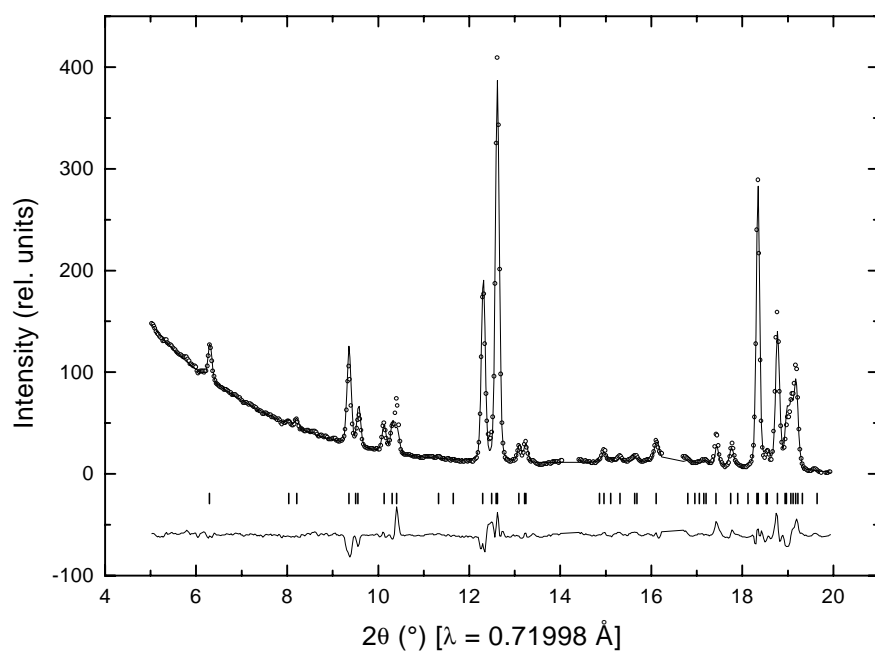
Results

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

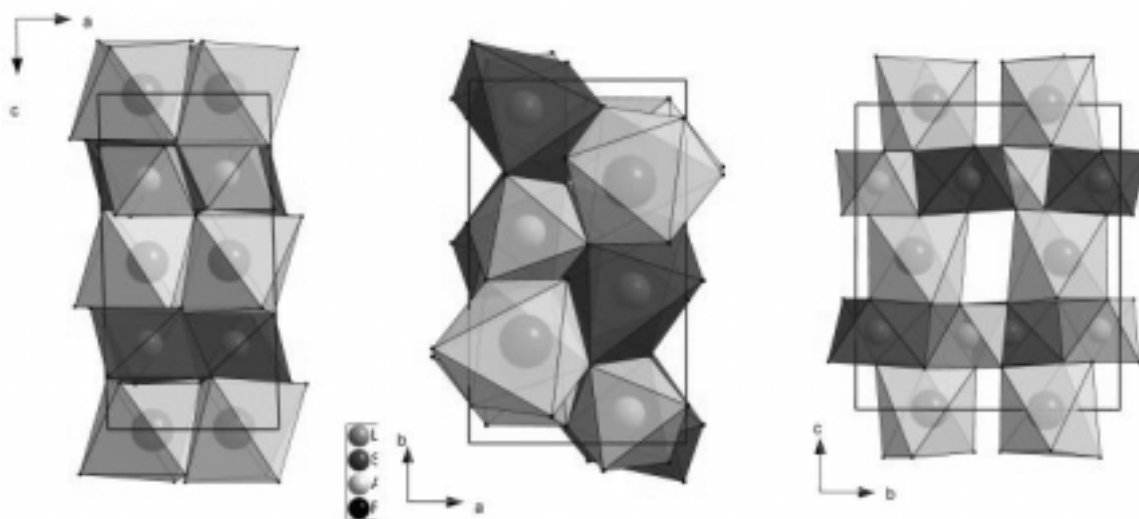
Grzechnik, A., Dmitriev, V., Weber, H.-P., Gesland, J.-Y., van Smaalen, S. (2004) – The crystal structures of pressure-induced LiSrAlF_6 -II and LiCaAlF_6 -II – J. Phys.: Condensed Matter **16**, 1033

Abstract

Crystal structures of LiCaAlF_6 -II and LiSrAlF_6 -II (both $P2_1/c$, $Z = 4$) occurring at high pressures and room temperature were studied with synchrotron angle-dispersive x-ray powder diffraction in diamond anvil cells. The structure of LiSrAlF_6 -II stable between 1.6 and 3.0 GPa was solved with a global optimisation algorithm and group theory considerations, and refined with the Rietveld method in the rigid-body approximation. It is a distorted variant of the ambient pressure polymorph (LiSrAlF_6 -I, $P\bar{3}1c$, $Z = 2$), in which each cation occupies a deformed octahedral site. LiCaAlF_6 transforms to this monoclinic polymorph II above about 7 GPa. The differences in the high-pressure behaviours of LiCaAlF_6 and LiSrAlF_6 are discussed considering the ionic radii.



Observed, calculated, and difference x-ray powder patterns for LiSrAlF₆-II ($P2_1/c$, $Z = 4$) at 1.6 GPa. Vertical markers indicate Bragg reflections. The 2θ regions 14.05-14.4° and 16.25-16.7°, in which two reflections due to argon are observed, were excluded from the Rietveld refinement.



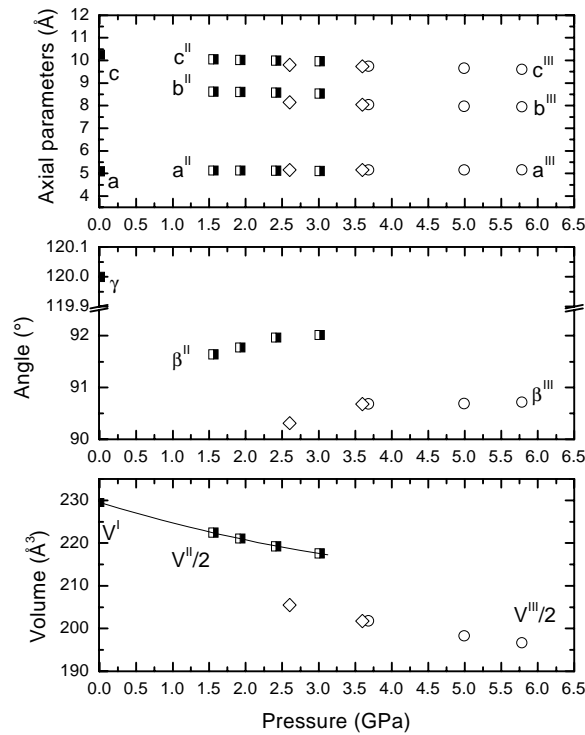
Crystal structure of $\text{LiSrAlF}_6\text{-II}$ ($P2_1/c$, $Z = 4$).

Grzechnik, A., Dmitriev, V., Weber, H.-P., Gesland, J.-Y., van Smaalen, S. (2004) $-\text{LiSrAlF}_6$ with the LiBaCrF_6 -type structure – *J. Phys.: Condensed Matter* **16**, 3005

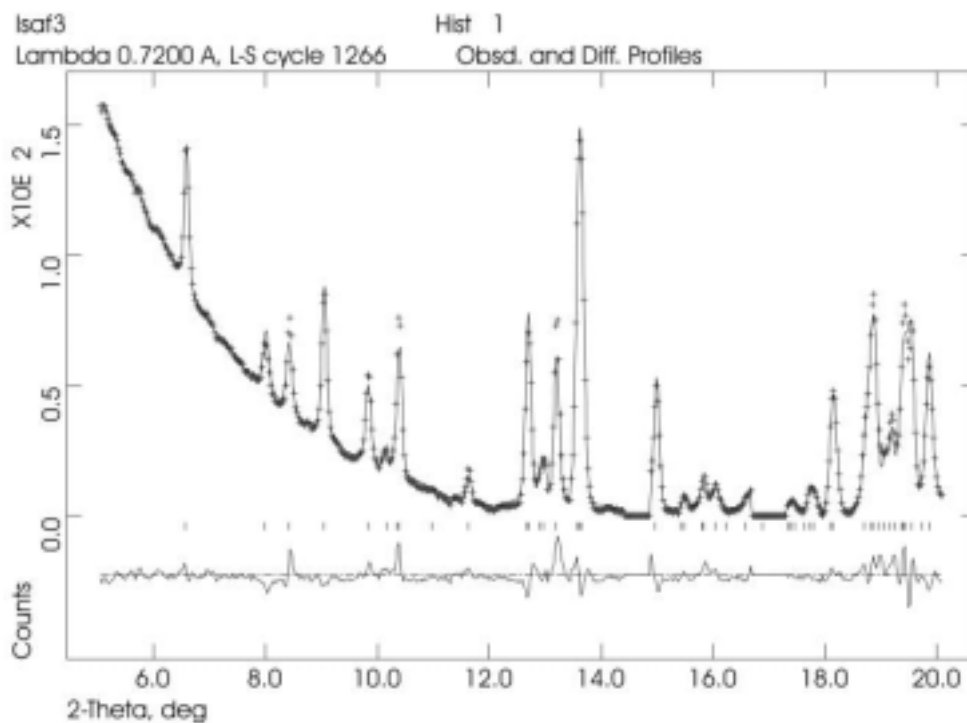
Abstract

The crystal structure of $\text{LiSrAlF}_6\text{-III}$ ($P2_1/c$, $Z = 4$) occurring above 3.0 GPa at room temperature was studied with synchrotron angle-dispersive x-ray powder diffraction in a diamond anvil cell. It was solved by combining a global optimisation and a topological analysis with the Rietveld method using rigid-body AlF_6 geometrical constraints. $\text{LiSrAlF}_6\text{-III}$, related to LiBaCrF_6 ($P2_1/c$, $Z = 4$), is built of deformed SrF_{12} icosahedra within a three-dimensional framework of corner-sharing distorted AlF_6

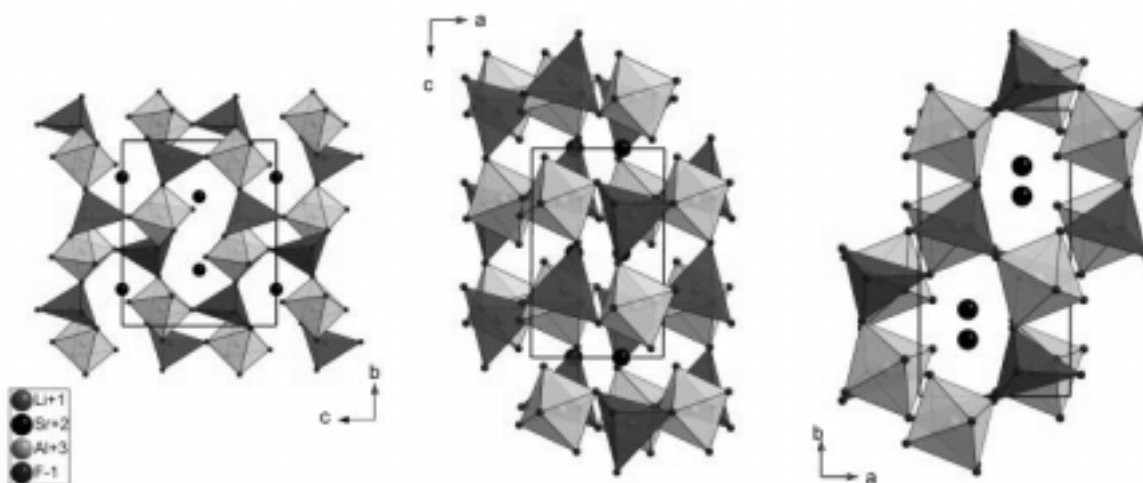
octahedra and LiF_4 tetrahedra, whereas the low-pressure phases I ($P\bar{3}1c$, $Z = 2$) and II ($P2_1/c$, $Z = 4$) have cations exclusively in distorted octahedral coordinations. The pressure-induced changes of the coordination polyhedra in the series LiSrAlF_6 -I, LiSrAlF_6 -II, to LiSrAlF_6 -III are similar to the differences in coordination polyhedra due to the increase of the ionic radii of the Sr^{+2} and Ba^{+2} cations in LiSrAlF_6 -I and $\text{LiBaM}''\text{F}_6$ ($\text{M}'' = \text{Al, Ga, Cr, V, Fe, or Ti}$) at ambient conditions. These observations are discussed on the basis of the high-pressure high-temperature systematics in AB_2X_6 compounds.



Pressure dependence of lattice parameters and unit cell volumes in LiSrAlF_6 up to 6.0 GPa. Full, half open, and open symbols stand for the LiSrAlF_6 -I, LiSrAlF_6 -II, and LiSrAlF_6 -III polymorphs, respectively. Open circles and diamonds stand for the data upon compression and decompression, respectively. For clarity, the unit cell volumes of the monoclinic phases are divided by a factor of two. The line represents the equation-of-state fit to the unit cell volumes of LiSrAlF_6 -I and LiSrAlF_6 -II.



Observed, calculated, and difference x-ray powder patterns for $\text{LiSrAlF}_6\text{-III}$ ($P2_1/c$, $Z = 4$) at 2.6 GPa as obtained after the final Rietveld refinement. Vertical markers indicate the positions of Bragg reflections. The 2θ regions $14.40\text{-}14.88^\circ$ and $16.70\text{-}17.30^\circ$, in which two reflections due to argon are observed, were excluded from the Rietveld refinement.



Projections of the crystal structure of $\text{LiSrAlF}_6\text{-III}$ ($P2_1/c$, $Z = 4$).

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