



Beamline: BM01B	Experiment title: High-temperature study of colquiriite laser hosts	Experiment number: 01-01-655
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	Shifts: 18	Local contact(s): H. Emerich
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Report:

Aims of the experiment and scientific background

Solid state lasers are usually based on oxide compounds containing rare earth elements [1]. The key property of a material to be useful as a laser-host is its high luminescence efficiency. Fluorides are of interest as laser-host materials because of their large band gaps and low phonon energies resulting in lower multiphonon emission rates and high luminescence efficiencies when compared to oxides. Furthermore, they are stable with respect to a radiation damage and they have small non-linear refractive indices [1,2]. LiYF_4 is already a commercially used host material for laser systems. Several other rare-earth doped fluorides exhibit a luminescence output comparable to the LiYF_4 phosphor [3-6]. They could also serve as solid state lasers or be useful for up-conversion laser action [7-9].

The *colquiriite* $\text{LiMM}'\text{F}_6$ ($\text{M} = \text{Ca}$ or Sr ; $\text{M}' = \text{Al}$, Ga , or Cr) family of fluoride compounds is considered to be the most promising for optical applications [1-10]. The crystal structure of LiCaAlF_6 ($P\bar{3}1c$, $Z = 2$) is an ordered derivative of the Li_2ZrF_6 type ($P\bar{3}1m$, $Z = 1$) [11]. Each cation occupies a deformed octahedral site. The fluorine atoms are in a hexagonal-close-packed array. The polyhedral distortions in $\text{LiMM}'\text{F}_6$ have been correlated with the sizes of the M and M' cations [9,11,12]. 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 [12].

Preliminary studies of the temperature dependence of lattice parameters in LiCaAlF_6 and LiSrAlF_6 at the temperature range 298-600 K [12] indicated that both materials have highly anisotropic thermal expansion, with the c parameter decreasing with increasing temperature. The electron spin resonance of Cr^{3+} in LiSrAlF_6 and LiSrGaF_6 at the temperature range 270-470 K showed that the magnitude of the zero-field splitting $|D|$ is bigger in LiSrGaF_6 , as a result of rotations of the trigonal F faces [13]. Unlike in LiSrAlF_6 , the $|D|$ parameter in LiSrGaF_6 decreases with increasing temperature. Such a behavior can be explained considering the opposite sign of thermal expansion coefficient of the c axis. The anisotropic thermal expansion indicates a high sensitivity against thermal shocks and thermal gradients in *colquiriites* [10]. The thermal conductivity in these fluorides is smaller than the one in oxide crystals and leads to higher temperature gradients during crystal growth and laser action. The heat produced within the crystals during the application as laser hosts can lead to cracking.

This project aimed to elucidate the structural origin of the anisotropic thermal expansion in *colquiriites* $\text{LiMM}'\text{F}_6$ ($M = \text{Ca}$ or Sr ; $M' = \text{Al}$ or Ga) by measuring their powder x-ray patterns as a function of temperature at ambient pressure. It was a supplement to the previous proposal about the structural stability of these materials at high pressures and high temperatures (HS2179).

Results

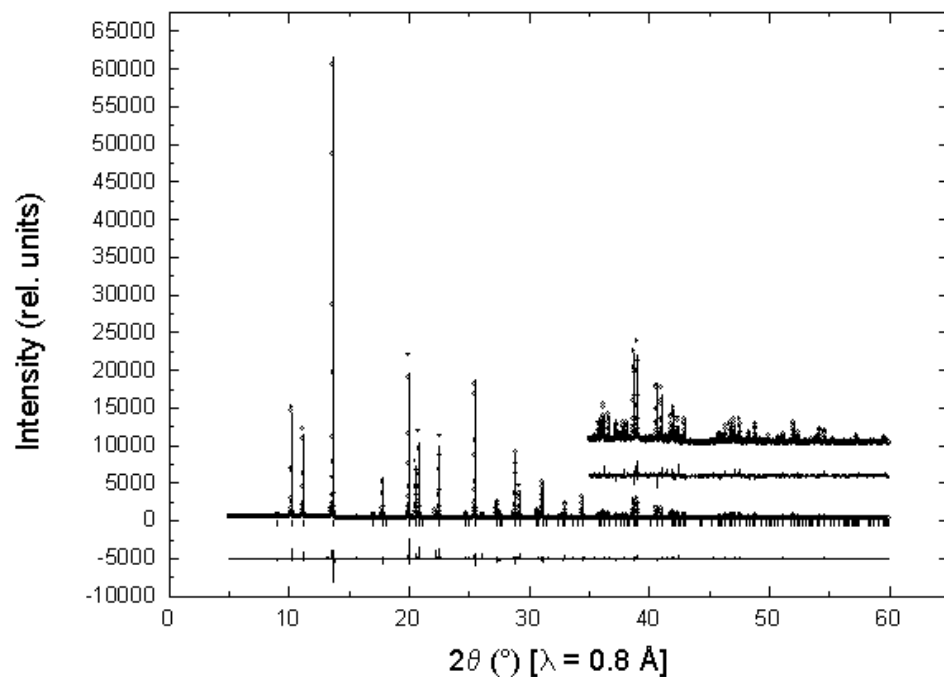
The results of this project have been published in J. Phys. Condens. Matter:

Grzechnik, A., Dmitriev, V., Weber, H.-P., Gesland, J.-Y., Friese, K. (2004) – Anisotropic thermal expansion in LiCaAlF_6 and LiSrAlF_6 – J. Phys.: Condensed Matter **16**, 5769

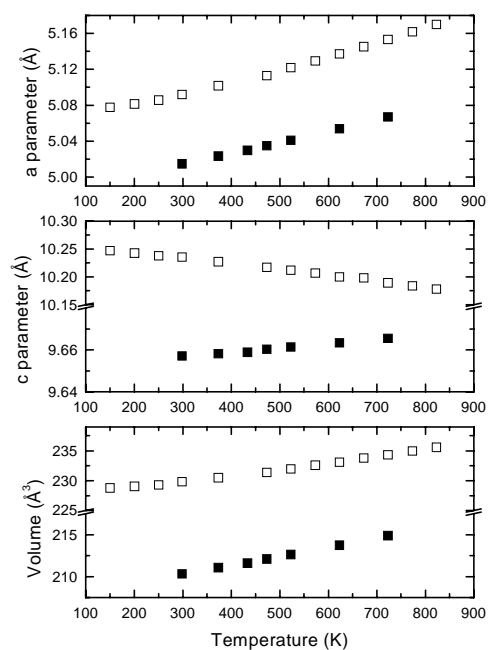
Abstract

High-temperature behaviour of LiSrAlF_6 and LiCaAlF_6 , both $P\bar{3}1c$ and $Z = 2$, was studied with high-resolution synchrotron angle-dispersive x-ray powder diffraction in the temperature ranges 150 to 823 K and 298 to 723 K, respectively. No phase transitions were detected. The temperature dependencies of structural parameters and octahedral distortions are obtained with the Rietveld method. Both materials have highly anisotropic thermal expansion, with the c parameter in LiSrAlF_6 decreasing with increasing temperature. Our observations on the temperature evolution of various structural parameters, like interatomic distances, angles, distortions, and polyhedral volumes indicate that the negative thermal expansion along the c axis in LiSrAlF_6 arises from concerted angular distortions around the Sr and Al atoms and diminished F...F interatomic distances in the SrF_6 slabs. The SrF_6 slab

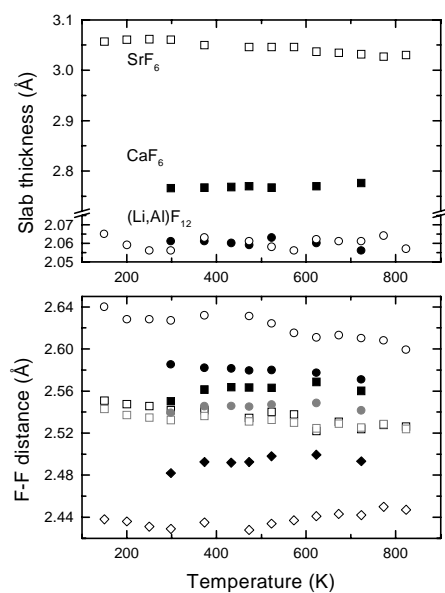
contracts with increasing temperatures because of the diminishing F-Sr-F octahedral angles. The CaF_6 layer becoming thicker and relatively temperature insensitive angular distortions do not result in anomalous negative thermal expansion in LiCaAlF_6 .



Observed, calculated, and difference x-ray powder diffraction patterns for LiSrAlF_6 at 823 K as obtained after the final Rietveld refinement. Vertical markers indicate the positions of Bragg reflections. The insert shows the patterns in the 2θ range 35-60° magnified five times.



Temperature dependence of lattice parameters and unit cell volumes in LiSrAlF₆ (open symbols) and LiCaAlF₆ (solid symbols).



Temperature dependence of non-bonded F...F distances and of thicknesses of octahedral slabs along the *c* axis in LiSrAlF₆ (open symbols) and LiCaAlF₆ (solid symbols). The gray symbols stand for the average F...F distances.

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