



	Experiment title: Measurement of the complete scattering of the light up-conversion material NaLuF ₄ and of NaYF ₄	Experiment number: 01-02-859
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Shifts: 9	Local contact(s): Dmitry Chernyshov, Phil Pattison	<i>Received at ESRF:</i>
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Report:

α -NaLuF₄: We have been investigating the full diffraction pattern of the light up-conversion material "cubic" α -NaLuF₄, a different phase from the previously studied hexagonal β -NaLnF₄ analogues [1]. Understanding the local structure of such materials, as well as the average structure, is an important step towards understanding and controlling the light up-conversion process and potentially being able to synthesize better materials of this type. Data collected during on BM01A (SNBL) at the ESRF in Nov. 2008 & June 2009 (reports HS-3639 & CH-2798) from different parts of the crystalline solid obtained from the synthesis in the melt reveal diffraction patterns that are richly populated with information: Bragg peaks, satellite peaks from commensurate modulation, evidence of 6-fold twinning and diffuse scattering. Two phases were detected. The diffraction pattern of phase I includes satellite reflections, while phase II does not exhibit satellite reflections and has a different pattern of diffuse scattering. The acquisition of good synchrotron data was an essential step in the project upon which we have based our subsequent analyses and attempts to model the structure. The current experiment recorded additional data for phase I at 100, 150, 200 and 295 K in order to follow the temperature evolution of the ADPs and unravel the site occupations and displacements of the atoms in the modulated structure from their positions in the cubic average structure published for NaLuF₄ [2].

A large amount of time was spent integrating the data sets before we could commence to model the structures, because the twinning and overlap of reflections severely complicated the usual data integration procedures and many trials with different settings were required. The average structural model for both phases based on the 6-fold twinned main reflections used a pseudo-tetragonal orthorhombic unit cell, space group *Cmmm*. The average structure has been interpreted and refined in terms of an orthorhombic version of the CaF₂ structure. Refinement in JANA [3] using only the main reflections allowed us to establish the twin volume fractions and the overall chemical composition of the material, which proved to be very close to the expected composition, Na₅Lu₉F₃₂, derived from powder diffraction in 1966 [2]. Considering only the positions of the heavy atoms in the asymmetric unit of this unit cell, the average structure may be described equally well in two different ways; essentially there are two different origin choices which lead to different numbers of independent metal atom sites in the asymmetric unit. The sites for the metal atoms are occupied to various extents by Na⁺, Lu³⁺ and vacancy. However, only one of the alternate models is chemically meaningful in terms of the coordination geometry of the metal atoms and the M-F distances. Restraints on the site occupation factors were required to avoid illogical occupancies and to maintain the overall chemical stoichiometry. Correlation between site occupation and atomic displacement parameters (ADPs) is strong and

hinders full anisotropic refinement of the F-atoms. The residual electron density in the difference Fourier maps was interpreted in terms of disordered fluorine atoms. The results are similar for all temperatures at which data were collected (100, 150, 200, 295 K). While the two phases have the same structure in terms of atomic positions, the occupancies of the various metal sites differ significantly (Fig. 1). This has consequences for the distortions of the F-atom positions, which tend to want to be closer to Lu^{3+} than to Na^+ and may be one of the contributions behind the modulated structure and satellite reflections observed for phase I.

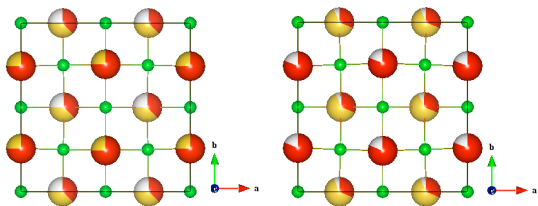


Fig. 1. The average structure of phase I (left) and phase II (right) in the pseudo-tetragonal unit cell, refined using the "main" reflections. The positions of the fluorine atoms are shown in green and the occupancies of the metal ion sites are shown in red (Lu), yellow (Na) and grey (vacancy).

Next, the modulation in the phase I structure was modelled in the five times larger C-centred orthorhombic supercell using the satellite reflections only (Fig. 2). Refinements using both satellite and main reflections were not fruitful because of the difficulty in properly scaling these two classes of reflections; the satellites have no overlaps with those of the other twin domains, whereas the main reflections do. Modelling the contents of the five-fold supercell is a very complex process, as the mixed $\text{Na}^+/\text{La}^{3+}/\text{vacancy}$ sites involve both positional and occupancy displacements from the average structure in the smaller unit cell. The phases of the superstructure reflections were determined by band-flipping implemented in the program SUPERFLIP [4-6]. The reconstructed difference electron densities show two distinct commensurately modulated parallel columns of cations: one with varying $\text{Na}^+/\text{Lu}^{3+}/\text{vacancy}$ occupancy and one with positional displacement of the ions from the average structure positions. Interestingly, two different solutions with equal probability result from band-flipping on the superstructure reflections. These two solutions differ only in the details of positional and occupational modulation. Although the two distinct solutions refine reasonably well to convergence, bond valence calculations suggest one solution is chemically more meaningful than the other. This is consistent with the conclusions described above for the two possible solutions involving the small pseudo-tetragonal cell.

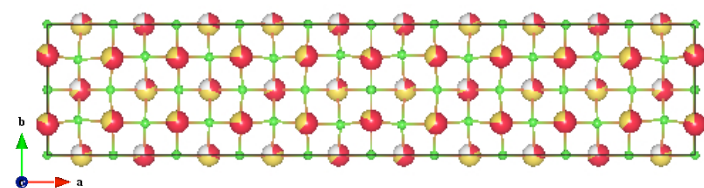


Fig. 2. The final 5-fold modulated structure of phase I, refined using the superspace approach. The positions of fluorine atoms are shown in green and the occupancies of the metal ion sites are shown in red (Lu), yellow (Na) and grey (vacancy).

In summary, we have now successfully elucidated the average disordered crystal structures of the two discovered phases of $\alpha\text{-NaLuF}_4$. The crystals of both phases are 6-fold twins and the structure of phase I is additionally commensurately modulated. In this study it was shown that non-trivial data integration methods and use of non-crystallographic absence conditions play a crucial role for optimal intensity extraction in the case of rare 6-fold pseudo-merohedral twinning. Structure solution and refinement based solely on the superstructure reflections and the information from SUPERFLIP difference electron density maps was successfully tested for the first time. It was also shown in this study that bond valence calculations are an important aid in selection the most likely model when structural refinement does not converge to a single solution. Furthermore, the practical challenges presented in integrating the highly twinned data and deriving models for modulated structure have contributed an advance to the skills set available for dealing with very complex crystallographic problems. The diffuse scattering in the structures has not been analysed, but may be a result of the strain in the twin boundaries and possible occupational and positional disorder which may correlate with the light up-conversion properties of the material. We have now realised that a successful quantitative investigation of the diffuse scattering is likely to be extremely difficult because the twinning makes it hard to deduce the true sources of the diffuse signals.

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