	Experiment title: Measurement of diffuse scattering and accurate structure factors of the light up-conversion materials $NaLuF_4$ and $NaYF_4$	**Experiment number**: HS-3639
Beamline: BM01A	**Date of experiment**: from: 13 Nov. 2008 to: 16 Nov. 2008	**Date of report**: 19.2.2009
Shifts: 9	**Local contact(s)**: Phil Pattison, Dmitry Chernyshov	*Received at ESRF:*

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Report:

Facilities used: MAR-345 detector for all measurements, wavelength 0.7335 Å, 11 data sets collected.

$NaLuF_4$: Four different crystals from different parts of the ampoules obtained from the melt using the Bridgman technique[1]; for each a fast data collection to record accurate Bragg intensities, plus a slow data collection to record accurate satellite intensities and diffuse scattering intensity; all measurements at RT.

$NaYF_4$: One sample, one measurement at room temp.

Aspirin: One sample, test measurement at 140 K

We are studying various phases of "cubic" $NaLuF_4$ and $NaYF_4$ obtained from the melt. Their diffraction patterns exhibit *m*3*m* symmetry (or pseudo *m*3*m*) and primitive or face-centred lattices. Initial measurements on in-house diffractometers revealed diffraction patterns of different parts of the obtained ampoules are richly populated with information: Bragg peaks, satellite peaks and weak diffuse scattering (DS, Fig. 1a). Some in-house data sets based only on Bragg intensities show evidence for occupational or positional disorder and unreasonably high extinction. The aim of the beamline experiments was to obtain better Bragg and satellite intensities and a proper assessment of the DS using crystals of a small size to minimize absorption problems.

$NaYF_4$: The very strong fluorescence observed for this compound with MoKα radiation (0.7107 Å) on a laboratory diffractometer makes detection of diffuse scattering difficult. At the wavelength chosen, 0.7335 Å, absorption for $NaYF_4$ is minimised (Y absorption edge is at 0.728 Å). The reduced fluorescence and background obtained at the wavelength used on BM01A allowed us to visualise the scattering patterns more clearly. Only Bragg reflections could be observed and there was no evidence of diffuse scattering or satellite peaks. We should be able to model the structure from the Bragg data alone.

$NaLuF_4$: Crystal 1. From near the end of the melt ampoule. Fig. 1a shows the richness of the scattering already obtained from MoKα sealed tube data. However, the additional information visible in reconstructions from the beamline data is astonishing (Fig. 1b). The diffraction patterns appear at first glance to have cubic symmetry, but a careful and detailed analysis of reciprocal space maps shows:

- The crystals do not have cubic symmetry, but tetragonal at the most, as the reflections along some lines in reciprocal space are not collinear, but alternate slightly each side of the mean line (Fig. 1a).
- The reciprocal space maps of this α-$NaLuF_4$ sample show satellite reflections indicating a commensurately modulated structure (Fig. 1a,b). If the cubic unit cell is transformed to *C*-tetragonal, the satellites align along unit cell vectors with a q-vector of 0.2.
- If the satellites are treated as Bragg peaks, one can derive an orthorhombic cell with space group *Cmmm*. We haveintegrated the satellite intensities and deleted saturated Bragg intensities. The structure could be solved easily in the 5-fold supercell using Superflip[2] and an initial comparison with the average structure derived from the "cubic" Bragg data showed close agreement of atomic positions and modulation of the site occupations of the shared Na/Lu sites in one column through the structure and possible positional displacements of similar sites in other columns through the structure. Subsequent treatment of the satellite data in terms of modulation vectors will simplify refinement.
- The apparent cubic lattice symmetry and systematic reflection "presences" in the tetragonal setting can be explained in terms of 6-fold twinning.
- The additional reflections in Fig. 1b are interpreted as arising from a second phase. Further evidence for this is seen in the reconstructions made from data from the other $NaLuF_4$ crystals taken from other parts of the melt ampoule (see below).
- The α-$NaLuF_4$ sample seems identical with one characterised in 1966 by powder diffraction for which no structural model was reported.[3]

$NaLuF_4$: Crystal 2. A second crystal of α-$NaLuF_4$ taken from another part of the melt ampoule shows main reflections analogous to the first sample (Fig. 1c), but the satellites are differently positioned and the diffuse scattering patterns differ. This suggests mixed phases with different ratios in the two crystals. Similar observations were made with the third and fourth crystal of $NaLuF_4$, thus demonstrating that the phase composition of the melt ampoule various continuously with the position along the ampoule.

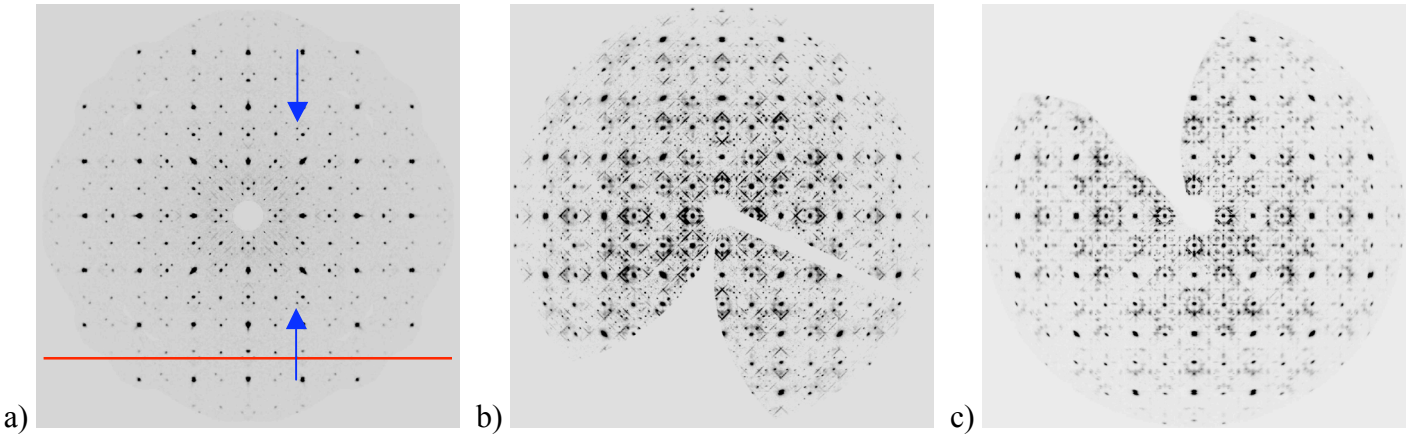

Fig. 1. *a*) The (0*kl*) layer from crystal 1 of α-$NaLuF_4$ on our in-house diffractometer, showing Bragg peaks, satellite peaks and very weak diffuse scattering. The reflections above the red line are not collinear indicating the presence of more than one reciprocal lattice. A row of satellite reflections is indicated by two arrows. *b*) Data taken from the same crystal on beamline BM01A shows extensive diffuse scattering and reflections from at least one additional phase. *c*) The (*h*0*l*) layer from α-$NaLuF_4$ crystal 2 on beamline BM01A.

The surprising results here – because they were unexpected – are twofold: (a) the discovery of six-fold twinning simulating the cubic structure postulated earlier,[2] and (b) the discovery of quite sharp satellite reflections. The latter indicate that partial ordering of the Na^+ and the Lu^{3+} ions predominates over a random distribution of these ions.

1. K. Krämer, University of Bern, private communication, 2008.
2. L. Palatinus, G. Chapuis, *J. Appl. Crystallogr*. **40** (2007) 786.
3. R.E. Thoma, H. Insley, G. M.Hebert, *Inorg. Chem*. **5** (1966) 1222.