

Electron Density Distribution and Rietveld Refinement on KNiF₃ Powder Diffraction Data

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The high resolution powder diffraction data ($\sin\theta/\lambda \sim 1.10 \text{ \AA}^{-1}$) at 300K and at 10K are successfully collected. Both data are refined by Rietveld method using Jana2000 program. The crystal data, atomic coordinates, and thermal parameters are listed in Table 1 and Table 2. The powder patterns and their refinement profiles for both temperatures data are displayed in Fig.1 and Fig.2, respectively. Electron density distributions obtained by applying maximum entropy method to both data are shown in Fig.3. The density along Ni-F is about $0.65(3) \text{ e/\AA}^3$, which is compared to the density at bond critical point of 0.39 e/\AA^3 obtained by single crystal result and that of 0.43 e/\AA^3 based on periodic DFT calculation.

Table 1 KNiF₃ powder refinement results

Formula	KNiF ₃	KNiF ₃
Formula Weight	154.80	154.80
λ (Å) / E (KeV)	0.55 / 22.5421	0.55 / 22.5421
Temperature (K)	300	10
Space Group	Cubic, P m -3 m	Cubic, P m -3 m
a (Å)	4.01879 (5)	4.01408 (3)
V (Å ³)	64.9065 (8)	64.6783 (5)
F(000)	74	74
2 θ (deg)	75	73
No. of meas. points	6561	6366
Parameters	32	32
Limiting Indices	$0 \leq h \leq 6$	$0 \leq h \leq 6$
	$0 \leq k \leq 4$	$0 \leq k \leq 4$
	$1 \leq l \leq 8$	$1 \leq l \leq 8$
No. of unique reflns. / obs. reflns. (>3 $\sigma(I)$)	104/87	100/85
R _p ; wR _p	2.54%; 4.21%	2.60%; 4.17%
R _f (obs); R _f (all)	2.74%; 3.03%	2.13%; 2.27%
wR _f (obs); R _f (all)	1.88%; 1.88%	1.77%; 1.77%

Table 2 Atomic Coordinate and Thermal Parameters

	x	y	z	Uiso (RT)	Uiso (LT)
Ni	0.5	0.5	0.5	0.0056(4)	0.0046(2)
K	0	0	0	0.0114(7)	0.0089(4)
F	0.5	0.5	0	0.0099(11)	0.0077(6)

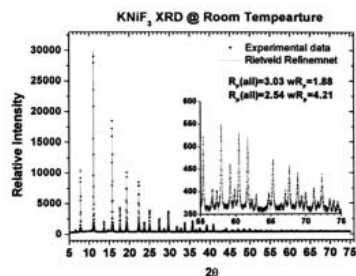


Fig. 1 Refinement of room temperature data

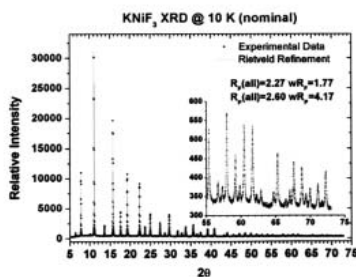


Fig.2 Refinement of low temperature data

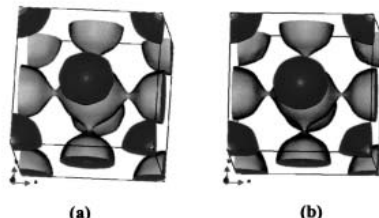


Fig. 3 Isosurface of electron density at (a) RT (b) 10K data with cutoff value at 0.65 e/\AA^3 . The Ni, K, and F are located on center, corner and face respectively.
 Ref: I. H. Tanaka, M. Takata, E. Nishibori, K. Kato, T. Iishi, and M. Sakata, J. Appl. Cryst. (2002) Vol. 35, 282-286

In-situ XRD study of porous SiO₂ films

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Surfactant templated porous materials exhibit long range ordered structures. The films of these materials have many applications in semiconductor and optical-electronic fields. In such a template approach, the interesting self-assembly process occurring between the surfactant and the inorganic silica phase leading to the final mesostructured hybrid material can be studied by in-situ 2D GIXD experiment.

The 2D in-situ GIXD investigation was performed on high-flux BL12B2 beamline at SPring-8. High quality X-ray beam with a 2D detector (off-line IP detector) was used to monitor the formation of liquid crystal mesophase due to solvent evaporation. It is very important to know how the liquid crystals form and transform into different phases. This behavior allows one to follow the structural formation of the mesostructured hybrid films during dip coating.

One set of experiments results was taken as the example, the 2D X-ray diffraction patterns are given in Figure at different times after deposition. In the following figures, one can clearly see that there is no organization in the first 10 s and that a diffraction ring and diffraction points appear after 1 min. This diffraction ring is due to the organization of the cylindrical micelles into domains that are not well-aligned with the surface of the film, but with the *c* axis randomly oriented, as suggested by the continuity of the diffraction ring.

The pattern does not change from 1 min to 3 min of the acquisition. However, the diffraction points disappear after 4 min. This indicates that the well-aligned 2D hexagonal structure was transform to randomly oriented.

Some experiments under different conditions were also done and these 2D GIXD patterns will be analyzed to find out the mechanism during mesophase formation.

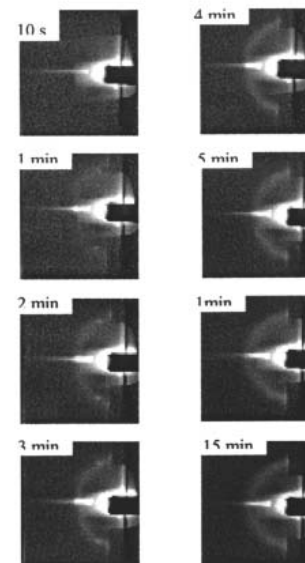


Fig. Two-dimensional PXRDX patterns showing the structural evolution of the film during solvent evaporation.