Crystal structure of two modifications of ammonium trifluoro nickelate(II), NH_4NiF_3

C. Plitzko, M. Strecker

Universität Hannover, Institut für Anorganische Chemie, Callinstr. 9, D-30167 Hannover, Germany

and G. Meyer

Universität Köln, Institut für Anorganische Chemie, Greinstr. 6, D-50939 Köln, Germany

Received June 17, 1996, transferred to 2nd update of database ICSD in 1997, CSD-No. 402540 and 402541

1. Crystal structure of the cubic low temperature modification of ammonium nickel trifluoride, NH_4NiF_3 -I

Source of material: NH_4NiF_3 -I in the cubic (low temperature) modification was obtained from nickel powder and NH_4HF_2 (molar ratio 1:1.5) at 573 K (four weeks) in a sealed Monel metal container. The yellow powder contains many square yellow plates (see ref. 1).

NH_4NiF_3 -I crystallizes like KNiF_3 (see ref. 2) in the cubic CaTiO_3 type of structure. The $[\text{NiF}_6]$ octahedra share common corners with Ni^{2+} -F distances of 204.38(14) pm to form a three-dimensional network. The Ni^{2+} - Ni^{2+} distances are 408.8(3) pm. H positions of NH_4^+ are not determined.

$\text{F}_3\text{H}_4\text{NNi}$, cubic, $Pm\bar{3}m$ (No. 221), $a = 4.088(3)$ Å, $V = 68.3$ Å³, $Z = 1$, $R(F) = 0.026$, $R_w(F^2) = 0.045$.

Table 1. Parameters used for the X-ray data collection

Crystal:	yellow, square plate, size 0.05 x 0.20 x 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	67.10 cm ⁻¹
Diffractometer:	STOE IPDS
Scan mode:	20 plates, $\Delta\phi = 5^\circ$
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	55.84°
$N(hkl)_{\text{unique}}$:	32
Criterion for I_o :	$I_o > 2\sigma(I_o)$
$N(\text{param})_{\text{refined}}$:	5
Program:	SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	1b	1/2	1/2	1/2	0.0123(7)	U_{11}	U_{11}	0	0	0
F	3c	1/2	1/2	0	0.018(2)	U_{11}	0.013(3)	0	0	0
N	1a	0	0	0	0.017(3)	U_{11}	U_{11}	0	0	0

2. Crystal structure of the hexagonal high temperature modification of ammonium nickel trifluoride, NH₄NiF₃-II

Source of material: NH₄NiF₃-II in the hexagonal (high temperature) modification was obtained from nickel powder and NH₄HF₂ (molar ratio 1:2) at 673 K (four weeks) in a sealed Monel metal container in the presence of a tungsten sheet on which the green crystals grew (see ref. 3).

NH₄NiF₃-II crystallizes like RbNiF₃ (see ref. 4) in the hexagonal BaTiO₃ type of structure. Two [NiF₆] octahedra share a common face forming a double octahedron [Ni₂F₉] with Ni²⁺-F(2)⁻ distances of 201.1(2) pm (6x) and Ni²⁺-F(1)⁻ distances of 203.8(2) pm (6x). These double octahedra share common corners with [NiF₆] octahedra to form a three-dimensional network. The Ni²⁺-F(1)⁻ distances are 202.6(1) pm (6x) in these ideal octahedra. The Ni²⁺-Ni²⁺ distance in the confacial bioctahedron is 275.0(1) pm. The H positions are not determined.

F₃H₄NNi, hexagonal, *P6₃/mmc* (No. 194), *a* = 5.8456(3) Å, *c* = 14.3563(3) Å, *V* = 424.9 Å³, *Z* = 6, *R*(*F*) = 0.024, *R_w*(*F*²) = 0.083.

Table 3. Parameters used for the X-ray data collection

Crystal:	green, rectangular plate, size 0.05 x 0.20 x 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	66.48 cm ⁻¹
Diffractometer:	Siemens-Stoe
Scan mode:	profile fitted $\omega/2\theta$
<i>T_{measurement}</i> :	293 K
$2\theta_{\max}$:	80.1°
<i>N(hkl)_{unique}</i> :	554
Criterion for <i>I</i> ₀ :	<i>I</i> ₀ > 2 σ (<i>I</i> ₀)
<i>N(param)_{refined}</i> :	21
Program:	SHELXL-93

Table 4. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ni(1)	2 <i>a</i>	0	0	0	0.0127(2)	<i>U</i> ₁₁	0.0132(3)	<i>U</i> ₁₁ /2	0	0
Ni(2)	4 <i>f</i>	1/3	2/3	0.84581(3)	0.0135(1)	<i>U</i> ₁₁	0.0129(2)	<i>U</i> ₁₁ /2	0	0
F(1)	6 <i>h</i>	0.5181(2)	2 <i>x</i>	1/4	0.0210(7)	0.0154(8)	0.0163(7)	<i>U</i> ₂₂ /2	0	0
F(2)	12 <i>k</i>	0.8342(2)	2 <i>x</i>	0.07898(9)	0.0216(5)	0.0170(6)	0.0195(6)	<i>U</i> ₂₂ /2	0.0028(2)	2 <i>U</i> ₁₃
N(1)	2 <i>b</i>	0	0	1/4	0.018(1)	<i>U</i> ₁₁	0.019(2)	<i>U</i> ₁₁ /2	0	0
N(2)	4 <i>f</i>	1/3	2/3	0.0953(3)	0.0188(8)	<i>U</i> ₁₁	0.019(1)	<i>U</i> ₁₁ /2	0	0

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for financial support.

References

- Plitzko, C.: Neue komplexe Ammoniumfluoride und Fluorid-Ammoniakate durch Umsetzung von Metallen mit Ammonium- und Hydraziniumfluoriden. Dissertation, University of Hannover, Germany 1996.
- Lule, A.; Schmitz-DuMont, O.: Struktur und Remissionsspektren der Ammoniumfluoroniccolate. *Z. Anorg. Allg. Chem.* **389** (1972) 1-10.
- Strecker, M.: Synthese von Fluoriden mit Ammoniumfluoriden und Polytetrafluorethylen. Dissertation, University of Hannover, Germany 1994.
- Babel, D.: Die Kristallstrukturen der hexagonalen Fluoroperowskite. *Z. Anorg. Allg. Chem.* **369** (1969) 117-130.
- Sheldrick, G. M.: SHELXL-93, a program for refining crystal structures. University of Göttingen, Germany 1993.