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Li_2NiF_4: Hydrothermal Synthesis and Crystal Structure

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Single crystals of Li_2NiF_4 are obtained by hydrothermal synthesis in HF solutions. The material is cubic (space group $Fd3m$, $a = 8.318(2)$ Å). The crystal structure, solved from single-crystal diffraction data ($R = 0.0303$, $R_w = 0.0316$), confirms the inverse spinel structural type previously proposed from powder data. © 1989 Academic Press, Inc.

Introduction

Li_2NiF_4 (*1*), Li_2ZnF_4, and Li_2CuF_4 (*2*) are the only fluorides reported to adopt the spinel structure. Li_2NiF_4 was found to be of the inverse type on the basis of a powder diffraction work, single crystals being not available by classical methods. In the course of the investigation of the LiF–NiF_2 system by hydrothermal synthesis in HF aqueous solutions, we isolated single crystals of Li_2NiF_4. This fact incited us to reexamine the crystal structure on the basis of single-crystal diffraction data.

Preparation

Single crystals of Li_2NiF_4 are grown by hydrothermal synthesis (*3*), in a sealed platinum tube, from concentrated HF aqueous solutions. Typical conditions of crystal growth are listed in Table I. After cooling, the solid was rapidly washed with ethanol and filtered. X-ray diffraction analysis of the resulting mixture revealed that three kinds of crystals were present: LiF, NiF_2, and Li_2NiF_4. The crystals of the latter phase are light green octahedra.

Structure Resolution

A small crystal of approximate size $3 \times 3 \times 3 \times 10^{-6}$ mm^3 was chosen for the structure determination. Table II gathers the condition of the data collection with a four-circle diffractometer.

The cell parameter was refined from the positions of 30 reflections with $2\theta \approx 30°$. Because of the small value of the absorption factor and the good agreement observed between a set of equivalent intensities—less than 10% discrepancy between the 24 equivalent intensities from the 335 reflection—we did not apply absorption corrections. The observed limiting condition for the possible reflections—$0kl$ with $k + l = 4n$—led to the possible space groups $Fd3m$ and $Fd3$.

All the calculations were performed with SHELX76 (*4*). Atomic scattering factors

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TABLE I

Li_2NiF_4: OPERATING CONDITIONS OF CRYSTAL GROWTH

Volume of platinum tube: 2.69 ml
Filling rate: 0.50
HF 40% volume: 1.22 ml
$[Li_2NiF_4]$: 5 mole/liter
P_{initial} (RT): 950 bars
Heating rate: 300°/hr
Temp. max. (T_f): 625°C
Stay at T_f: 24 hr
Cooling rate: 20°/hr
P_{final} (T_f): 2500 bars

TABLE II

CONDITIONS OF THE DATA COLLECTION (SIEMENS AED2)

Li_2NiF_4
Molecular weight: 148.58 g
Space group: $Fd3m$
$a = 8.318(3)$ Å
$V = 575.5$ Å^3, $Z = 8$, $\rho_{\text{calc}} = 3.43\ \text{g} \cdot \text{cm}^{-3}$
Radiation: $MoK\alpha$ (graphite monochromatized)
$\mu(MoK\alpha) = 66.92\ \text{cm}^{-1}$
$T = 20°C$
Scanning: $\omega/2\theta$
Angular range: $2° < 2\theta < 80°$
Part of reciprocal space explored: $0 \leq h \leq 14$
$0 \leq k \leq 10$
$0 \leq l \leq 8$
Total number of reflections measured: 122
Number of independent reflections with $\sigma(I)/I < 0.33$ used for the refinement: 84

and $\Delta f'$ and $\Delta f''$ were from "International Tables for X-Ray Crystallography" (*5*). In the space group $Fd3m$ (origin $3m$), we started with the model of Rudörff *et al.* (*1*), i.e., Li on 8a positions (tetrahedral sites), Li and Ni statistically on 16c positions (octahedral sites), and F on 32e positions. With this model and isotropic thermal motion for all atoms, the factors R and R_w dropped to 0.0373 and 0.0428, respectively. The introduction of the anisotropic thermal motion led to the values of 0.0303 and 0.316 for R and R_w, respectively (84 independent reflections). The weighting scheme was $w = 1.2375/(\sigma^2(F) - 1173 \times 10^{-6} \times F^2)$ and the secondary extinction parameter took the value $x = 477 \times 10^{-5}$. Other calculations were made in order to check the possibility of the simultaneous presence of Li and Ni on the two kinds of cationic positions, they were clearly unsuccessful. Calculations were then done in the space group $Fd3$ and did not improve the results of the first refinement. Table III gathers the best set of the adjustable parameters.[1]

The distances Li–F and (Li–Ni)–F—1.912(1) and 2.018(2) Å, respectively—are very close to the sum of the ionic radii—1.875 and 2.01 Å—corresponding to a tetrahedral coordination for Li and an octahedral one for (Li, Ni) (*6*).

TABLE III

BEST SET OF CRYSTALLOGRAPHIC PARAMETERS (×10^4) WITH THE e.s.d. IN PARENTHESES

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq} (Å^2)
Li	1250	1250	1250	135(17)						1.06
Li Ni	5000	5000	5000	94(3)	94(3)	94(3)	−13(1)	−13(1)	−13(1)	0.74
F	2577(1)	2577(1)	2577(1)	108(3)	108(3)	108(3)	−2(2)	−2(2)	−2(2)	0.85

Note. The vibrational coefficients relate to the expression: $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

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[1] A list of F_o and F_c values is available on request to J.-L.F.

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