SHORT-FORMAT PAPERS

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Structure of Lithium Nickel Phosphate

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Abstract. $LiNiPO_4$, $M_r = 160.60$, orthorhombic, *Pnma*, $a = 10.0317$ (1), $b = 5.8539$ (1), $c = 4.6768$ (1) Å, $V = 274.65$ (1) Å^3, $Z = 4$, $D_x = 3.884$ g cm^{-3}, $F(000) = 312$, λ(Cu $K\alpha_1$) = 1.54056 Å, $\mu = 144.36$ cm^{-1}, $R_{wp} = 11.15\%$, $R_{ex} = 9.25\%$, $\chi^2 = 1.47$ for 31 basic variables with 3699 observations corresponding to 128 reflections. The structure of the title compound has been refined by Rietveld analysis of X-ray powder diffraction data. $LiNiPO_4$ adopts an olivine-related structure, *viz.* hexagonal close packed oxygen with Li and Ni in half the octahedral sites and P in 1/8 of the tetrahedral sites. The X-ray powder diffraction pattern of lithium nickel phosphate has appeared previously as JCPDS file No. 32-578.

Experimental. $LiNiPO_4$ was prepared as a polycrystalline powder by solid-state reaction between Li_2CO_3, NiO and $NH_4H_2PO_4$. Stoichiometric quantities of the starting materials were ground together in an agate mortar and pestle for 15 min. After drying, the resulting mixture was placed in a gold boat. The sample was heated in a muffle furnace at 573 K for 2 h and then at 923 K for another 2h to decompose the phosphate and carbonate, respectively. This was followed by 36 h at 1023 K with one intermediate regrinding after 18 h. The final product was quenched to room temperature. Phase purity was determined by X-ray powder diffraction photographs using a Stoe Guinier camera with Cu $K\alpha$ radiation. Weight-loss measurements confirmed the combined loss of ammonia, carbon dioxide and water.

High-resolution X-ray powder diffraction data were collected at room temperature on a Stoe Stadi/*P* diffractometer in symmetric transmission mode using Ge-monochromated Cu $K\alpha_1$ radiation. Data were collected in the 2θ range 15–90° in steps of 0.02°. Calibration was achieved by using an external Si standard. The structure was refined using the program *GSAS* (Larson, Von Dreele & Lujan, 1990) with a pseudo-Voigt function used to model the peak shape. Scattering factors for neutral atoms assumed and correction for real and anomalous dispersion applied (*International Tables for X-ray Crystallography*, 1974, Vol. IV). Weights $1/y$(obs.). No absorption correction was applied and no correction for preferred orientation. A simultaneous polynomial background fit was carried out with five variable parameters. A correction for the monochromator polarization fraction was also applied. Polyhedral projections were generated using *STRUPLO* (Fischer, 1985).

The structural parameters of $LiMnPO_4$ (Geller & Duran, 1960) were used as a starting model for the Rietveld refinement. Scale and background parameters were refined initially followed in subsequent iterations by cell, zero point, peak shape, atomic and isotropic thermal parameters. Refinement terminated with $R_{wp} = 11.15\%$ $R_{ex} = 9.25\%$, maximum $\Delta/\sigma = 0.01$ for 31 basic variables and 3699 observables corresponding to 128 reflections. Refined atomic parameters are given in Table 1† with selected inter-

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† The numbered intensity of each measured point on the profile has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55851 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1024]

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Table 1. *Refined atomic parameters for* $LiNiPO_4$ *with e.s.d.'s in parentheses*

	Site	x	y	z	U_{iso}(Å^2 × 10^2)
Li	4(*c*)	0.0	0.0	0.0	2.8 (5)
Ni	4(*c*)	0.2756 (1)	0.25	0.9825 (3)	0.96 (5)
P	4(*c*)	0.0943 (2)	0.25	0.4167 (5)	0.81 (8)
O(1)	4(*c*)	0.1008 (5)	0.25	0.7427 (10)	0.3 (2)
O(2)	4(*c*)	0.4492 (5)	0.25	0.1978 (10)	0.4 (2)
O(3)	8(*c*)	0.1668 (4)	0.0439 (6)	0.2783 (7)	0.8 (1)

$R_{wp} = 11.15\%$; $R_{ex} = 9.25\%$; $\chi^2 = 1.47$.

Table 2. *Selected interatomic distances* (Å) *in* $LiNiPO_4$ *with e.s.d.'s in parentheses*

Li—O(1)	2.148 (3) × 2	Ni—O(3)	2.051 (3) × 2
Li—O(2)	2.097 (3) × 2	Ni—O(3')	2.135 (3) × 2
Li—O(3)	2.135 (4) × 2	P—O(1)	1.526 (5)
Ni—O(1)	2.082 (5)	P—O(2)	1.551 (6)
Ni—O(2)	2.012 (5)	P—O(3)	1.550 (4) × 2

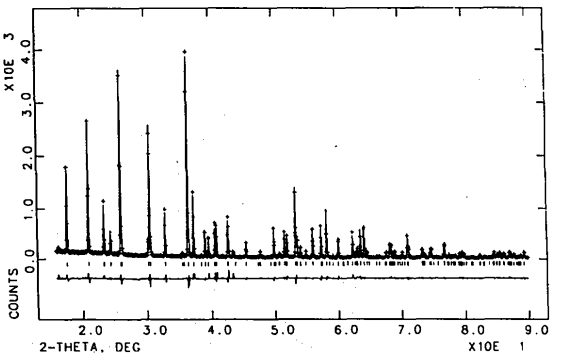

Fig. 1. Final difference profile plot for $LiNiPO_4$ showing observed (plus signs), calculated (line) and difference (lower) profiles.

atomic contact distances in Table 2. The final difference profile is shown in Fig. 1 with a polyhedral projection of the structure shown in Fig. 2.

Related literature. The structure of $LiNiPO_4$ is related to that of olivine, Mg_2SiO_4 (Megaw, 1973) and is essentially isostructural with $LiMnPO_4$ (Geller & Duran, 1960). $LiNiPO_4$ is one member of a large family of olivine-related structures of the type $ABPO_4$ where A and B are mono- and divalent cations, respectively. Other structure types are also adopted by phosphates of this stoichiometry depending on the relative size of the B cation: for example, $NaZnPO_4$ (Elammari, Durand, Cot & Elouadi, 1987), $NaCaPO_4$ (Ben Amara, Vlasse, Le Flem & Hagenmuller, 1983) and $LiCaPO_4$ (Lightfoot, Pienkowski, Bruce & Abrahams, 1991).

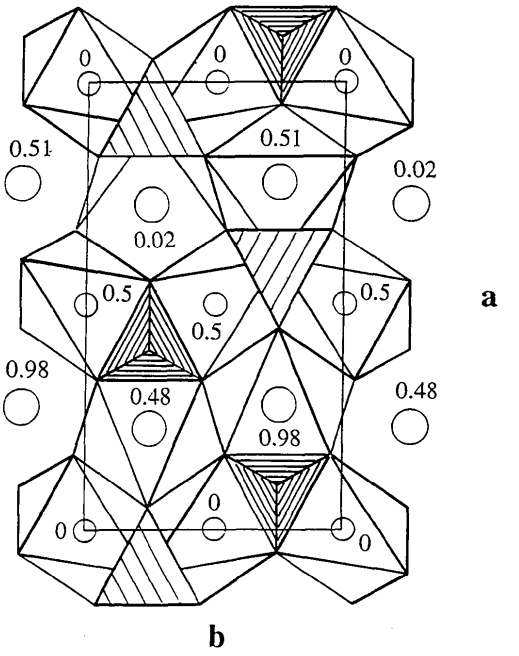

Fig. 2. Polyhedral projection of the $LiNiPO_4$ structure, with z coordinates given for Li (small open circles) and Ni (large open circles).

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References

BEN AMARA, M., VLASSE, M., LE FLEM, G. & HAGENMULLER, P. (1983). *Acta Cryst.* C**39**, 1483–1485.

ELAMMARI, L., DURAND, J., COT, L. & ELOUADI, B. (1987). *Z. Kristallogr.* **180**, 137–140.

FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.

GELLER, S. & DURAN, J. L. (1960). *Acta Cryst.* **13**, 325–331.

LARSON, A. C., VON DREELE, R. B. & LUJAN, M. JR (1990). *GSAS. Generalized Structure Analysis System.* Neutron Scattering Centre, Los Alamos National Laboratory, California, USA.

LIGHTFOOT, P., PIENKOWSKI, M. C., BRUCE, P. G. & ABRAHAMS, I. (1991). *J. Mater. Chem.* **1**, 1061–1063.

MEGAW, H. D. (1973). *Crystal Structures – a Working Approach*, pp. 249–254. London: W. B. Saunders.