BRIEF COMMUNICATIONS

The Crystal Structure of SrNi$_2$(PO$_4$)$_2$

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SrNi$_2$(PO$_4$)$_2$ is triclinic, with space group $P\bar{1}$, $Z = 2$, and cell parameters $a = 5.468(1)$ Å, $b = 6.667(1)$ Å, $c = 9.156(1)$ Å, $\alpha = 110.58(1)°$, $\beta = 100.87(1)°$, $\gamma = 98.01(1)°$. A full matrix least squares refinement led to $R = 0.032$, $R_w = 0.041$ for 2330 independent reflections. The structure is described from chains running along the b axis involving Ni(1)$_2$O$_{10}$ units formed from two Ni(1)O$_6$ octahedra sharing one edge, Ni(2)O$_5$ pyramids, and P(1)O$_4$ tetrahedra. These chains are connected by P(2)O$_4$ tetrahedra and weak Ni(2)–O(2) bonds leading to layers [Ni$_2$(PO$_4$)$_2$]$_x$ parallel to the (001) plane. Interleaved strontium cations ensure the cohesion between these sheets. © 1993 Academic Press, Inc.

Introduction

The mixed phosphates of strontium or barium and divalent metals (Mg,Ni,Cu,Zn) have been studied and characterized by different authors. Thus, in their investigation of the system Sr$_3$(PO$_4$)$_2$–Mg$_3$(PO$_4$)$_2$, Sarver *et al.* (*1*) have reported the existence of the solid solution Sr$_{3-x}$Mg$_x$(PO$_4$)$_2$ ($0.27 \leq x \leq 1.08$), isomorphous to β-Sr$_3$(PO$_4$)$_2$, and of the phosphate SrMg$_2$(PO$_4$)$_2$ with unknown crystal structure.

Moqine (*2*) and Boukhari *et al.* (*3*) have obtained the phosphate Sr$_3$Cu$_3$(PO$_4$)$_4$ isostructural with its homologous Ca$_3$Cu$_3$(PO$_4$)$_4$ (*4*). Their structures contain (CuCuCu) trimeric linear ions which possess exotic magnetic properties (*3, 5, 6*). Sarver *et al.* (*1*) have synthesized the solid solution Sr$_{3-x}$Zn$_x$(PO$_4$)$_2$, isotypical with the high temperature form of β-Sr$_3$(PO$_4$)$_2$, and the phosphate SrZn$_2$(PO$_4$)$_2$. The later has two allotropic varieties α and β with a transition at $T = 1035°$C (*1*). The crystalline structure of

TABLE I

CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT
PARAMETERS FOR $SrNi_2(PO_4)_2$

	Crystal data
Space group	$P\bar{1}$
Cell dimensions	$a = 5.458(1)$ Å
	$b = 6.649(1)$ Å
	$c = 9.136(1)$ Å
	$\alpha = 110.59(1)°$
	$\beta = 110.86(1)°$
	$\gamma = 98.04(1)°$
Volume	$V = 297.05$ Å^3
Z	2
	Data collection
Equipment	CAD-4 ENRAF-NONIUS
(MoKα (graphite monochromator)	0.7107 Å
Scan mode	$\omega - 2\Theta$
Scan width(°)	1. + 0.34 tan Θ
Θ range (°)	2–35
Standard reflections	$2\bar{1}2, 0\bar{1}\bar{2}, 1\bar{4}\bar{1}$
	measured every 200 refections (no decay)
Recording reciprocal space	$-8 \leq h \leq 8, -10 \leq k \leq 10, 0 \leq l \leq 14$
Number of measured reflections	2742
Number of reflections $I > 3\sigma(I)$	2446
Number of independent reflections (used in refinement)	2330
μ (cm^{-1}) (for $\lambda K\bar{\alpha} = 0.7107$ Å)	161
Transmission factor range	0.059–0.096
	Refinement
Number of refined parameters	119
$R \Sigma[|Fo| - |Fc|]/\Sigma|Fo|$	0.032
$Rw = [\Sigma w(|Fo| - |Fc|)^2/\Sigma|Fo^2|]^{1/2}$ with w = 1	0.041

α-$SrZn_2(PO_4)_2$ was determined by Hemon and Courbion (7).

On the other hand, the system Ba_3 $(PO_4)_2$–$Mg_3(PO_4)_2$ was studied by Hoffman (8), which reported the powder diagrams of $Ba_2Mg(PO_4)_2$ and $BaMg_2(PO_4)_2$. Regnault (9) has solved the structure of $BaCo_2(PO_4)_2$. Several papers report on the system Ba_3 $(PO_4)_2$–$Ni_3(PO_4)_2$ (10–14). The symmetry of the phosphate $BaNI_2(PO_4)_2$ is rhomboedral (R3) (10). Its magnetic behavior was studied (12, 14).

In the binary $Ba_3(PO_4)_2$–$Zn_3(PO_4)_2$ two phosphates were reported: $Ba_2Zn(PO_4)_2$ and $BaZn_2(PO_4)_2$ (8). From optical properties studies, Napijalo and Napijalo (13) con-

cluded that $SrNi_2(PO_4)_2$, $SrCo_2(PO_4)_2$, and $BaNi_2(PO_4)_2$ are isotypical.

We have isolated single crystals of $SrNi_2(PO_4)_2$. The present paper deals with the crystal structure of this phosphate, which is different from that of $BaNi_2(PO_4)_2$.

Preparation

The compound was prepared from NiO, $SrCO_3$, and $(NH_4)_2HPO_4$ (Merck > 99%) according to the stoichiometry

$$SrCO_3 + 2 NiO + 2(NH_4)_2 HPO_4 \rightarrow$$

$$SrNi_2(PO_4)_2 + \overrightarrow{CO_2} + \overrightarrow{4NH_3} + \overrightarrow{3H_2O}.$$
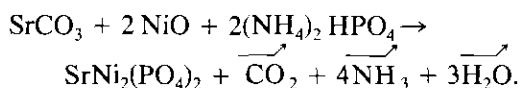
The mixture was preheated in a platinum

TABLE II

POSITIONAL PARAMETERS ($\times 10^5$ FOR Sr, Ni; $\times 10^4$ FOR P AND O) AND ISOTROPIC EQUIVALENT DISPLACEMENT PARAMETER ($\times 10^2$) FOR Sr Ni$_2$ (PO$_4$)$_2$

Atom	x	y	z	B_{eq}(Å^2)
Sr	75692(8)	79799(6)	55526(5)	55(1)
Ni(1)	14162(10)	85599(9)	5986(6)	39(1)
Ni(2)	49302(11)	41054(9)	15471(6)	54(1)
P(1)	6550(2)	−266(2)	1963(1)	35(2)
P(2)	1072(2)	5704(2)	2581(1)	32(2)
O(1)	1193(6)	4048(5)	919(4)	52(7)
O(2)	5029(6)	−2673(5)	814(4)	67(7)
O(3)	8787(6)	453(5)	1316(4)	48(7)
O(4)	4535(6)	1170(5)	1862(4)	57(7)
O(5)	1516(6)	8036(5)	2625(4)	60(7)
O(6)	−1458(6)	5111(5)	2984(4)	65(7)
O(7)	7497(6)	13(5)	3698(4)	62(7)
O(8)	3381(6)	5464(5)	3734(4)	61(7)

Note. Numbers in parentheses are estimated standard deviations in the last significant figures. The B_{eq} are defined by $B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$.

crucible at 900°C for 12 hr and fired at 1250°C for 24 hr.

Single crystals were obtained from the molten salt (1280°C) slowly cooled (10°C/hr) to ambient temperature. The yellowish crystals recovered were irregularly shaped.

Structure Determination

A crystal ground to a spherical shape (diameter 0.0270 cm) was selected for X-ray data collection. Weissenberg photographs indicate that the crystal belongs to the triclinic system. Intensities data collection was made on a CAD4-Enraf Nonius four-circle diffractometer. Table I gathers the experimental conditions. The unit cell parameters were refined from the positions of 25 reflections. The calculated volume is 297.05 Å^3, giving a calculated density, with $Z = 2$, of 4.42 g cm^{-3} (the experimental density is 4.44(5) g cm^{-3}).

Intensities were corrected for Lorentz-polarization effects and spherical absorp-

tion corrections were applied. The structure was solved by assuming the space group $P\bar{1}$. The Sr and Ni atoms were located by the heavy atom method. P and O coordinates were deduced from subsequent refinements and difference syntheses. The refinement of atomic parameters and anisotropic thermal motion for all atoms converged to the reliability factor $R = 0.032$ ($Rw = 0.041$). Scattering factors were taken from (*15*). The anomalous dispersion corrections were made according to Cromer and Liberman (*16*). The full matrix least squares refinements were performed with a local modification of SFLS-5 (*17*).

Atomic coordinates and equivalent isotropic temperature factors are reported in Table II.[1]

These results allow us to calculate intensity of powder X-ray diffraction lines and to refine unit cell parameters from the X-ray powder spectrum obtained with a SIEMENS D5000 diffractometer using monochromated Cu$K\bar{\alpha}$ radiation (Table III) and silicon as internal standard. The refined values are in good concordance with the results of single crystal measurements:

$a =$ 5.468(1) $b =$ 6.667(1) $c =$ 9.156(1)
$\alpha =$ 110.58(1) $\beta =$ 100.87(1) $\gamma =$ 98.01(1).

Structure Description

Table IV gives the main interatomic distances and angles (calculated with unit cell parameters refined from powder data). The structure of SrNi$_2$(PO$_4$)$_2$ can be described as a two dimensional framework of PO$_4$ tetrahedra and NiO$_{5-6}$ polyhedra linked by edges and vertices. These layers lying parallel to the ab plane at $x \approx 0$ are connected to each other by strontium ions (Fig. 1).

Figure 2 shows a layer projected onto the

[1] Lists of structure factors and anisotropic thermal motion parameters are available upon request from the authors.

TABLE III

Observed and Calculated X-Ray Powder Diffraction Pattern for $SrNi_2(PO_4)_2$

h k l	$2\Theta_{mes}$	$2\Theta_{cal}$	I_{obs}	I_{cal}
0 0 1	10.66	10.67	15.3	17.0
0 1 0	14.56	14.55	3.0	2.6
1 0 $\bar{1}$	17.56	17.56	6.0	6.0
1 $\bar{1}$ 0	19.74	19.73	11.6	12.5
0 1 $\bar{2}$	20.69	20.71	0.9	1.1
1 $\bar{1}$ 1	21.84	21.83	13.0	13.9
1 0 1	22.28	22.28	7.2	8.5
1 1 $\bar{1}$	22.64	22.64	4.3	5.5
1 $\bar{1}$ $\bar{1}$	23.11	23.11	11.1	9.8
1 1 $\bar{2}$	25.39	25.39	5.3	5.2
1 $\bar{1}$ $\bar{2}$	28.29	28.27	12.2	10.5
0 2 $\bar{2}$	28.88	28.86	100	100
0 1 $\bar{3}$	29.87	29.86	2.4	2.5
1 $\bar{1}$ 2	30.28	30.27	25.6	20.6
0 1 2	30.44	30.43	14.2	13.3
1 1 1	30.89	30.87	64.8	62.7
1 1 $\bar{3}$	31.87	31.86	11.6	10.6
0 0 3	32.39	32.39	7.2	8.3
1 0 $\bar{3}$	32.52	32.52	53.1	44.9
2 0 $\bar{1}$	33.14	33.13	40.7	40.2
2 $\bar{1}$ 0	34.10	34.11	31.3	27.2
1 2 $\bar{2}$	34.26	34.19	2.0	3.7
2 0 0		34.24		2.2
1 $\bar{2}$ 1	34.73	34.72	36.4	36.1
0 2 1	35.12	35.13	2.9	4.5
2 $\bar{1}$ 1	36.81	36.78	4.0	3.9
1 $\bar{1}$ 3	37.03	37.01	6.4	8.1
2 1 $\bar{1}$	37.78	37.78	3.0	3.9
2 1 $\bar{2}$	38.30	38.30	1.9	2.1
2 0 1	38.62	38.61	4.0	4.5
2 $\bar{1}$ $\bar{2}$	38.87	38.89	3.6	4.1
1 $\bar{1}$ $\bar{3}$	39.39	39.38	4.4	4.5
0 1 $\bar{4}$	40.14	40.13	17.0	14.8
0 1 3	40.79	40.76	3.2	3.1
2 $\bar{2}$ 1	40.86	40.85	11.1	12.7
0 3 $\bar{2}$	41.24	41.23	2.1	1.6
0 3 $\bar{1}$	41.51	41.50	1.4	1.4
0 2 $\bar{4}$	42.15	42.14	9.6	9.1
2 $\bar{1}$ 2	42.31	42.32	5.9	5.1
2 $\bar{2}$ $\bar{1}$	42.36	42.32	4.4	4.8
1 0 $\bar{4}$	42.58	42.59	2.0	1.5
1 $\bar{3}$ 2	43.06	43.05	8.4	8.1
1 2 1	43.32	43.35	18.0	9.3
2 $\bar{2}$ 2	44.12	44.10	7.4	8.1
0 3 0	44.63	44.65	6.2	5.1
2 $\bar{1}$ 3	45.45	45.44	14.1	8.1
2 0 2		45.46		8.4
2 $\bar{2}$ $\bar{2}$	46.21	46.22	9.7	5.5
1 $\bar{3}$ 3	46.77	46.75	1.2	2.3

TABLE III—Continued

h k l	$2\Theta_{mes}$	$2\Theta_{cal}$	I_{obs}	I_{cal}
1 $\bar{1}$ 4	47.02	47.02	4.6	3.2
1 $\bar{2}$ 4	47.51	57.51	7.5	4.4
2 1 $\bar{4}$	47.96	47.93	31.2	5.1
2 2 $\bar{3}$		47.93		9.0
1 3 $\bar{1}$		47.96		19.1
1 3 $\bar{3}$		48.00		4.2
2 $\bar{2}$ 3	50.60	50.56	2.5	2.7
3 0 $\bar{1}$		50.59		1.3
3 $\bar{1}$ $\bar{1}$		50.61		1.1
2 2 0	50.81	80.82	2.6	5.6
2 $\bar{3}$ 2	51.45	51.45	8.2	7.6
0 2 $\bar{5}$		51.50		1.4
0 1 4	51.80	51.81	9.2	9.0
1 2 $\bar{5}$	51.94	51.98	13.5	15.2
3 0 0	52.39	52.41	3.0	6.4
3 $\bar{1}$ 2	52.62	52.66	6.1	6.4
1 $\bar{3}$ 4	52.77	52.77	1.5	1.8
2 1 2	53.17	53.17	2.4	2.0
1 0 $\bar{5}$	53.50	53.51	8.6	2.2
2 $\bar{3}$ $\bar{1}$		53.55		6.0
3 $\bar{1}$ 1	54.04	54.06	3.8	2.9
2 $\bar{2}$ $\bar{3}$	54.30	54.27	0.6	0.9
2 $\bar{3}$ 3	55.72	55.73	3.7	4.1
2 1 $\bar{5}$	55.88	55.88	3.8	3.8

ab plane. In this layer two $Ni(1)O_6$ octahedra related by a symmetry center share an $O(3)$–$O(3)'$ edge to constitute a $Ni(1)_2O_{10}$ unit; square-pyramidal $Ni(2)O_5$ polyhedra link two $Ni(1)_2O_{10}$ units together by corner sharing through $O(1)$, $O(2)$, and $O(4)$ to form chains parallel to the a axis. The intrachain cohesion is reinforced by $P(1)O_4$ tetrahedra; one $P(1)O_4$ shares an edge $O(2)$–$O(4)$ with one NiO_6 octahedron of one $Ni(1)_2O_{10}$, an $O(3)$ atom with another $Ni(1)_2O_{10}$ unit and an $O(2)$ atom with one $Ni(2)O_5$ square pyramid. The fourth oxygen atom of the $P(1)O_4$ tetrahedron is not involved in the chains or layers formation and participates only in the interlayer cohesion via strontium ions.

Two parallel ribbons containing $Ni(1)_2O_{10}$ units and $Ni(2)O_5$ and $P(1)O_4$ polyedra are interconnected by weak $Ni(2)$–$O(2)$ bonds and $P(2)O_4$ tetrahedra. One $P(2)O_4$ tetrahedron shares three oxygen atoms with one ribbon and the fourth with another. If the

TABLE IV

Bond Distances (Å), Angles (°), and Valence Bonds (s) in $Sr_2Ni(PO_4)_2$

Ni(1) Octahedron / Ni(2) Octahedron

Ni(1)Octahedron		s	Ni(2) Octahedron		s
Ni(1)–O(1)$'_{010}$	1.963(3)	0.43	Ni(2)–O(1)	2.007(3)	0.39
O(2)$_{010}$	2.244(4)	0.20	O(2)$'_{100}$	2.039(3)	0.35
O(3)$_{\bar{1}10}$	2.091(4)	0.31	O(4)	2.064(4)	0.33
O(3)$'_{110}$	2.068(4)	0.33	O(6)	2.028(3)	0.36
O(4)$_{010}$	2.071(3)	0.32	O(8)	2.264(4)	0.19
O(5)	1.998(4)	0.39	O(2)$_{010}$	2.463(4)	0.11
<Ni(1)–O>	2.072(9)	1.98	<Ni(2)–O>	2.144	1.73

Sr polyhedron

		s			
Sr–O(3)$'_{211}$	2.905(3)	0.12	Sr–O(7)$_{010}$	2.516(4)	0.34
Sr–O(4)$'_{111}$	2.741(4)	0.19	O(7)$'_{211}$	2.681(3)	0.22
Sr–O(5)$'_{121}$	2.508(3)	0.35	O(8)	2.522(3)	0.34
Sr–O(6)$_{100}$	2.658(3)	0.23	O(8)$'_{111}$	2.611(4)	0.26
			<Sr–O>	2.643	2.05

P(1) tetrahedron / P(2) tetrahedron

P(1) tetrahedron		s	P(2) tetrahedron		s
P(1)–O(2)	1.576(3)	1.12	P(2)–O(1)	1.554(3)	1.19
O(3)	1.545(4)	1.22	O(5)	1.525(4)	1.28
O(4)	1.567(4)	1.15	O(6)	1.533(4)	1.25
O(7)	1.510(4)	1.34	O(8)	1.551(4)	1.20
<P(1)–O>	1.550	4.83	<P(2)–O> 1.541		4.92
O(2)–P(1)–O(3)	110.2(4)		O(1)–P(2)–O(5)	110.3(4)	
O(2)–P(1)–O(4)	103.8(4)		O(1)–P(2)–O(6)	112.1(4)	
O(2)–P(1)–O(7)	113.4(4)		O(1)–P(2)–O(8)	101.4(3)	
O(3)–P(1)–O(4)	109.6(4)		O(5)–P(2)–O(6)	110.7(4)	
O(3)–P(1)–O(7)	110.6(5)		O(5)–P(2)–O(8)	109.8(5)	
O(4)P(1)–O(7)	109.0(4)		O(6)–P(2)–O(8)	112.3(4)	
<O–P(1)–O>	109.4		<O–P(2)–O>	109.4	

Oxygen environment

		s			
O(1)–Ni(1)$'_{010}$	1.963(3)	0.43	O(5)–Sr$'_{121}$	2.508(3)	0.35
Ni(2)	2.007(3)	0.38	Ni(1)	1.998(4)	0.39
P(2)	1.554(3)	1.19	P(2)	1.525(4)	1.28
		2.00			2.02
O(2)–Ni(1)$_{0\bar{1}0}$	2.244(3)	0.20	O(6)–Sr$_{\bar{1}00}$	2.658(3)	0.28
Ni(2)$_{0\bar{1}0}$	2.463(4)	0.11	Ni(2)$_{\bar{1}00}$	2.028(3)	0.36
Ni(2)$'_{100}$	2.039(4)	0.35	P(2)	1.533(4)	1.25
P(1)	1.576(4)	1.12			1.89
		1.78			
O(3)–Sr$'_{211}$	2.905(3)	0.12	O(7)–Sr$_{0\bar{1}0}$	2.516(4)	0.34
Ni(1)$_{\bar{1}10}$	2.091(4)	0.31	Sr$'_{211}$	2.681(3)	0.22
NI(1)$'_{110}$	2.068(4)	0.33	P(1)	1.510(4)	1.34
P(1)	1.545(4)	1.21			1.90
		1.97			
O(4)–Sr$'_{111}$	2.741(4)	0.19	O(8)–Sr	2.522(3)	0.34
Ni(1)$_{0\bar{1}0}$	2.071(3)	0.32	Sr$'_{111}$	2.611(4)	0.26
Ni(2)	2.064(4)	0.33	Ni(2)	2.264(4)	0.19
P(1)	1.567(4)	1.14	P(2)	1.551(4)	1.20
		1.98			1.99

Note. O(n)$'_{pqr}$ represents atom O(n) to which the symmety $\bar{x}\,\bar{y}\,\bar{z}$ has been applied followed by a translation $p\vec{a} + q\vec{b} + r\vec{c}$.
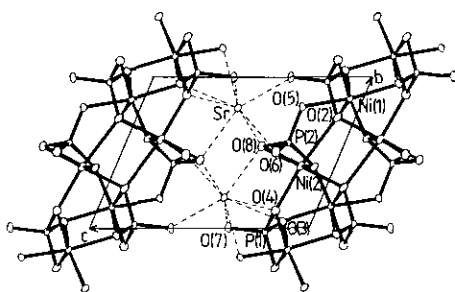
FIG. 1. Projection along a of the $SrNi_2(PO_4)_2$ structure.

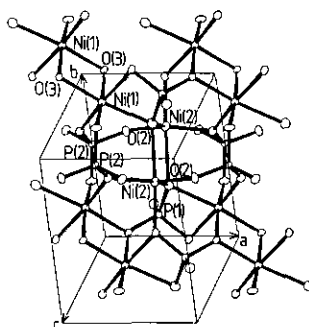FIG. 2. The $[Ni_2(PO_4)_2]_x$ layers parallel to the ab plane.

weak Ni(2)–O(2) bond is considered, the coordination around Ni(2) can also be described as a distorted octahedron and $N(2)_2O_{10}$ units are formed from two edge-sharing $Ni(2)O_6$ octahedra. Then the structure of $SrNi_2(PO_4)_2$ can be described as layers obtained from assemblage of Ni_2O_{10} units formed from two edge-sharing NiO_6 octahedra linked directly and by PO_4 tetrahedra.

Within the $Ni(1)_2O_{10}$ dimeric unit the nickel–nickel distance is 2.993(1) Å; the metal–metal distance within the $Ni(2)_2O_{10}$ unit is of course longer (3.448(1) Å). The phosphate tetrahedra are somewhat distorted with P–O distances ranging from 1.507 to 1.571 Å; the shortest P–O distance (1.507(4) Å) occurs with the O(7) atom which is not involved in a Ni–O bond. The strontium ions are eightfold coordinated with distances from 2.501 to 2.899 Å; the next nearest oxygen atom is an O(7) at 3.323(4) Å. The mean Sr–O distance (2.637 Å) is close to the distance calculated in $Sr_3(PO_4)_2$ (2.597 Å) (18). The Ni(1) octahedron is distorted with five distances ranging from 1.958 to 2.086 Å and a sixth, longer bond at 2.240(4) Å with the O(2) atom. The coordination polyhedron around Ni(2) is more distorted with four distances between 2.003 and 2.060 Å, one distance of 2.259(4) Å, and a longer distance of 2.457(4) Å with an O(2) atom; thus Ni(2) is five- or six-fold

coordinated. Even if sixfold coordination is considered, bond-length bond-strength calculations using the method of Brown and Shannon (19) and the data of Brown and Altermatt (20) give a value of 1.75 v.u. for Ni(2). In contrast, the value for Ni(1) (2.02 v.u.) is very good. In the same way, these calculations give acceptable values for oxygen atoms (ranging from 1.87 to 2.05 v.u.) except for the O(2) atom (1.79 v.u.). The coordination around Sr is well defined with a value of 2.08 v.u.

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