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Distrontium Nickel Orthophosphate

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Abstract

The Ni^{2+} cations in $Sr_2Ni(PO_4)_2$ occupy two sites of octahedral geometry and are separated by distances of greater than 4.8 Å [average Ni—O bond 2.08(2) Å]. Strontium shows eightfold coordination with irregular geometry and an average Sr—O distance of 2.64(2) Å.

Comment

Single-crystal X-ray analyses of orthophosphates $M_3(PO_4)_2$, where M is an alkaline-earth or bivalent transition metal, have been reported for α-$Ca_3(PO_4)_2$ (Mathew, Schroeder, Dickens & Brown, 1977), β-$Ca_3(PO_4)_2$ (Dickens, Schroeder & Brown, 1974), $Ca_3(PO_4)_2$ (high pressure; Roux, Loüer & Bonel, 1978), α-$Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ (Zachariasen, 1948), $Co_3(PO_4)_2$ (Anderson, Kostiner, Miller & Rea, 1975), $Ni_3(PO_4)_2$ (Calvo & Fagiani, 1975), $Cu_3(PO_4)_2$ (Shoemaker, Anderson & Kostiner, 1977), α-$Zn_3(PO_4)_2$ (Calvo, 1965), β-$Zn_3(PO_4)_2$ (Stephens & Calvo, 1967), $Fe_3(PO_4)_2$ (Kostiner & Rea, 1974), $Mg_3(PO_4)_2$ (Nord & Kierkegaard, 1968) and β'-$Mn_3(PO_4)_2$ (Stephens & Calvo, 1969).

Studies of mixed phosphates, $M'_xA_{3-x}(PO_4)_2$ (A = alkaline-earth metal and M' = divalent first-row transition element) are relatively uncommon and often do not include single-crystal data. However, the solid-state structures of $SrCo_2(PO_4)_2$ (Elbali, Boukhari, Holt & Aride, 1992), $BaNi_2(PO_4)_2$ (Cabrić, Zizić & Napijalo, 1982), α-$CaZn_2(PO_4)_2$ (Jakeman & Cheetham, 1988), $Ca_3Cu_3(PO_4)_4$ (Anderson, Kostiner & Ruszala, 1981), α-$SrZn_2(PO_4)_2$ (Hemon & Courbion, 1990) and $BaCo_2(PO_4)_2$ (Regnault, 1976) have been reported.

$Sr_2Ni(PO_4)_2$ exists in the solid state as sheets of PO_4^{3-} and Ni^{2+}, parallel to ($\bar{1}01$) and linked in the (001) direction by O—Ni interactions (Fig. 1). These linkages define tunnels extending parallel to (010) and containing the Sr^{2+} ions. Ni1 is situated on an inversion center [average Ni—O distance 2.09(2) Å] and Ni2 in a general position (average Ni—O length 2.0 Å); both display distorted octahedral geometry. The three Sr atoms of the asymmetric unit show eightfold coordination with average Sr—O distances of 2.64(2) Å. The geometry of PO_4^{3-} is approximately tetrahedral [average P—O distance 1.54(2) Å].

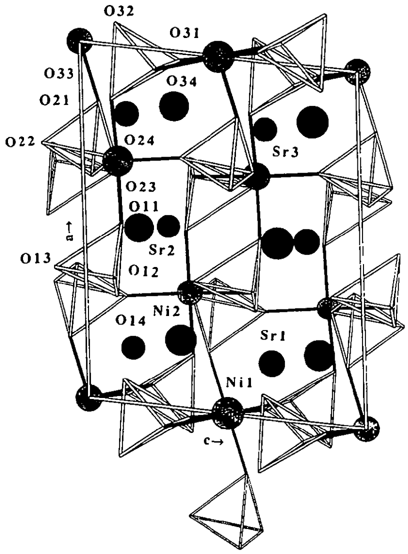

Fig. 1. Projection of $Sr_2Ni(PO_4)_2$ down the [010] axis.

This structure is intermediate between those of $Sr_3(PO_4)_2$ and $Ni_3(PO_4)_2$. The coordination number of strontium has changed from 12 and 10 in $Sr_3(PO_4)_2$ (Zachariasen, 1948) to eight. The Sr—O distances in $Sr_3(PO_4)_2$ (2.86, 2.66 Å) show the elongation expected with higher coordination. In $Ni_3(PO_4)_2$, Ni displays distorted octahedral geometry and the Ni—O distances are 2.078(2) and 2.084(2) Å.

Experimental

Crystal data

$Sr_2^{2+}Ni^{2+}(PO_4)_2^{3-}$
M_r = 423.89
Mo $K\alpha$ radiation
λ = 0.71069 Å

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Monoclinic
$P2_1/c$
$a = 11.631$ (7) Å
$b = 9.929$ (2) Å
$c = 8.990$ (2) Å
$\beta = 97.63$ (4)°
$V = 1029.1$ (7) Å^3
$Z = 6$
$D_x = 4.103$ Mg m^{-3}

Cell parameters from 15 reflections
$\theta = 10.48$-17.43°
$\mu = 182.32$ mm^{-1}
$T = 298$ K
Irregular chunk
$0.10 \times 0.10 \times 0.10$ mm
Yellow

Data collection

Syntex *P*3 automated diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{\rm min} = 0.68$, $T_{\rm max} = 0.84$
4363 measured reflections
4363 independent reflections
1616 observed reflections $[I > 3.0\,\sigma(I)]$

$R_{\rm int} = 0$
$\theta_{\rm max} = 30.0$°
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 97 reflections intensity variation: <5%

Refinement

Refinement on *F*
Final $R = 0.062$
$wR = 0.084$
$S = 0.42$
1616 reflections
179 parameters
$w = 1/\sigma(F)^2$
$(\Delta/\sigma)_{\rm max} = 0.64$

$\Delta\rho_{\rm max} = 0.80$ e Å^{-3}
$\Delta\rho_{\rm min} = 0.28$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Syntex-Nicolet *P*3 data collection package. Cell refinement: Syntex-Nicolet *P*3 data collection package. Data reduction: *DREAM* (Blessing, 1986). Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1980). Program(s) used to refine structure: *XRAY78* (Stewart, 1978). Molecular graphics: *CHEM3D* (Rubenstein & Rubenstein, 1987).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sr1	0.8109 (2)	0.2279 (2)	0.6622 (2)	4.8
Sr2	0.4931 (2)	0.6152 (2)	0.1964 (2)	5.5
Sr3	0.1528 (2)	0.3511 (2)	0.6644 (2)	4.1
Ni1	0.0000	0.0000	0.5000	3.8
Ni2	0.3252 (2)	0.3897 (3)	0.3735 (3)	2.2
P1	0.3739 (4)	0.8990 (5)	0.0626 (6)	1.7
P2	0.7124 (5)	0.5734 (6)	0.0085 (6)	3.6
P3	0.9566 (4)	0.9319 (6)	0.2117 (6)	4.2
O11	0.498 (1)	0.866 (2)	0.134 (2)	10.7
O12	0.344 (1)	1.048 (2)	0.101 (2)	6.7
O13	0.356 (12)	0.898 (2)	−0.112 (2)	4.0
O14	0.295 (1)	0.793 (2)	0.111 (2)	13.0
O21	0.836 (1)	0.518 (2)	0.063 (2)	5.8
O22	0.703 (1)	0.629 (2)	−0.146 (2)	12.4
O23	0.627 (1)	0.463 (2)	0.031 (2)	8.3
O24	0.684 (2)	0.686 (2)	0.115 (2)	6.6
O31	0.976 (1)	0.844 (2)	0.359 (2)	4.5
O32	1.063 (1)	0.916 (1)	0.130 (2)	4.0
O33	0.848 (1)	0.882 (2)	0.109 (2)	8.0
O34	0.944 (1)	1.074 (2)	0.272 (2)	6.6

Table 2. *Geometric parameters* (Å, °)

Ni1—O34$^{\rm i}$	2.19 (2)	Sr1—O31$^{\rm vii}$	2.61 (1)
Ni1—O31$^{\rm i}$	2.00 (2)	Sr1—O13$^{\rm iv}$	2.56 (1)
Ni1—O34$^{\rm ii}$	2.19 (2)	Sr1—O14$^{\rm iv}$	2.68 (2)
Ni1—O31$^{\rm ii}$	2.00 (2)	Sr1—O14$^{\rm ii}$	2.52 (2)
Ni1—O21$^{\rm iii}$	2.07 (2)	Sr1—O23$^{\rm viii}$	2.98 (2)
Ni1—O21$^{\rm iv}$	2.07 (2)	Sr1—O32$^{\rm vii}$	2.64 (1)
Ni2—O22$^{\rm v}$	2.03 (2)	Sr1—O34$^{\rm vi}$	2.62 (1)
Ni2—O12$^{\rm vi}$	2.12 (2)	Sr1—O21$^{\rm viii}$	2.63 (1)
Ni2—O13$^{\rm vi}$	2.14 (2)	Sr2—O24	2.53 (2)
Ni2—O24$^{\rm iv}$	2.03 (1)	Sr2—O23	2.74 (2)
Ni2—O11$^{\rm iv}$	2.08 (2)	Sr2—O11	2.55 (2)
Ni2—O33$^{\rm iv}$	2.04 (2)	Sr2—O14	2.92 (2)
P1—O11	1.54 (2)	Sr2—O23$^{\rm v}$	2.44 (2)
P1—O12	1.57 (2)	Sr2—O12$^{\rm iv}$	2.53 (1)
P1—O13	1.55 (1)	Sr2—O13$^{\rm vi}$	2.51 (2)
P1—O14	1.50 (2)	Sr2—O11$^{\rm iv}$	2.90 (2)
P2—O21	1.56 (2)	Sr3—O31$^{\rm ii}$	2.44 (1)
P2—O22	1.49 (2)	Sr3—O12$^{\rm vi}$	2.58 (2)
P2—O23	1.51 (2)	Sr3—O33$^{\rm iv}$	2.48 (2)
P2—O24	1.53 (2)	Sr3—O21$^{\rm ii}$	2.76 (2)
P3—O31	1.58 (2)	Sr3—O22$^{\rm iv}$	2.79 (2)
P3—O32	1.52 (2)	Sr3—O24$^{\rm ii}$	2.59 (2)
P3—O33	1.54 (2)	Sr3—O32$^{\rm ix}$	2.54 (1)
P3—O34	1.54 (1)	Sr3—O34$^{\rm ix}$	2.83 (2)

Symmetry codes: (i) $x-1, y-1, z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-1, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $1-x, 1-y, -z$; (vi) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (vii) $2-x, 1-y, 1-z$; (viii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $x-1, \frac{3}{2}-y, \frac{1}{2}+z$.

The title compound was obtained by the direct fusion of a very pure ($\gg$99%) mixture of $SrCO_3$, $NiCO_3$ and $(NH_4)_2HPO_4$ (stoichiometry 3:3:4), heated to 1173 K to effect decarbonation. The mixture was then heated in a platinum crucible until fusion at 1573 K before being cooled slowly (10 K h^{-1}). The powder thus obtained contained two types of crystals distinguishable by their color (light and dark yellow). The light-yellow crystals correspond to $Sr_2Ni(PO_4)_2$.

The data were collected using a variable scan rate and a scan width from 1.2° below $K\alpha_1$ to 1.2° above $K\alpha_2$. Refinement was performed using full-matrix least-squares methods.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55925 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1013]

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Structure of Hexagonal V_3S_4 Determined at Three Different Temperatures

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Abstract

Hexagonal trivanadium tetrasulfide, V_3S_4, is isotypic with Nb_3Se_4 and $Tl_xV_6S_8$. In contrast to $Tl_xV_6S_8$, the hexagonal channels are empty. Quasi-one-dimensional metal zigzag chains lie parallel to the crystallographic c axis with V—V distances of 2.864 (1) Å within the chains and 3.120 (1) Å between the chains. The crystal structure was determined at 295, 170 and 100 K. The contraction of the lattice with falling temperature is isotropic. V_3S_4 is metastable and transforms into the monoclinic V_3S_4 modification at elevated temperatures.

Comment

Compounds with the hexagonal Nb_3Se_4 structure (Smeggil, 1971) are of great interest because of their quasi-one-dimensional metallic properties (Amberger, Polborn, Grimm, Dietrich & Obst, 1978; Biberacher & Schwenk, 1980; Ishihara & Nakada, 1982, 1983; Ishihara, Nakada, Suzuki & Ichihara, 1984; Bensch, Koy & Biberacher, 1992*a*). During a systematic study of compounds with the Nb_3Se_4 structure with respect to their physical properties, hexagonal V_3S_4 was prepared by a topotactic redox reaction of $K_{0.7}V_6S_8$ with water. $K_{0.2}V_6S_8$ was reported not to be hygroscopic (Bronsema & Wiegers, 1987). In contrast, $K_{0.7}V_6S_8$ is highly air sensitive and reacts immediately with water to give V_3S_4. The preparation of the compound by a topotactic redox reaction using $Tl_xV_6S_8$ ($x = 0.8$) (Vlasse & Fournes, 1976) as starting material leads to products which contain small amounts of Tl ($x \simeq 0.03$) (Bensch, Koy & Wesemann, 1992). $Tl_xV_6S_8$ ($x = 0.8$)

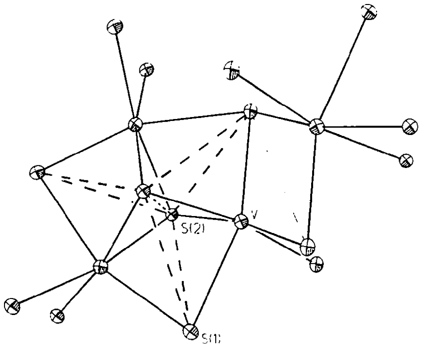

Fig. 1. A triple unit of three face-sharing VS_6 octahedra connected by a common edge to the neighbouring VS_6 octahedron. The common faces are indicated by the broken double lines, the common edge by the broken single line. Probability ellipsoids have been drawn at the 75% probability level ($T = 295$ K).

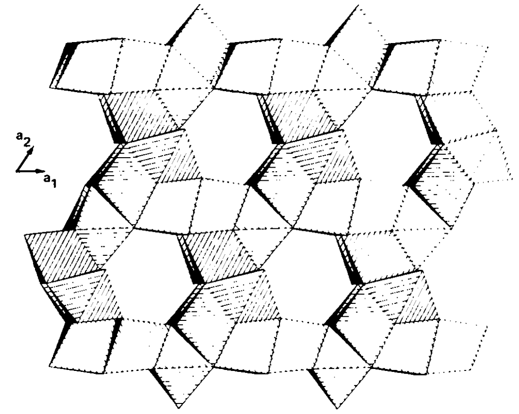

Fig. 2. Polyhedral representation of the structure of hexagonal V_3S_4.

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