

Investigations of the Structure of $\text{SrNiZn}(\text{PO}_4)_2$ The Nickel Distribution within the Lattice of Related Compounds

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Abstract

SrNiZn(PO₄)₂ is isostructural to SrNi₂(PO₄)₂. The lattice parameters are: $a = 5.4560(10)$, $b = 6.7110(10)$, $c = 9.1820(10)$, $V = 110.600(10)$, $Z = 101.100(10)$, $P-1$, $Z=2$ for 1009 independent reflections, $R_1 = 6.98$, $wR = 7.03$. The structure consists of sheets made of edge-sharing $[\text{NiO}_6]$ and $[\text{ZnO}_5]$ polyhedra. In the title compound, Ni ions are forming dimers $[\text{Ni}_2\text{O}_{10}]$ with short $d_{\text{Ni-Ni}}$ of 3.006 Å.

INTRODUCTION

Preparation and crystal structures of orthophosphates $\text{M}_3(\text{PO}_4)_2$ or $\text{T}_3(\text{PO}_4)_2$ ($\text{M} = \text{Alcaline-earth}$, $\text{T} = 3d\text{-transition divalent metal including Zn}$) have been studied for a long time in some detail (El Bali¹ and references therein). During the last decades mixed orthophosphates $\text{M}_{3-x}\text{T}_x(\text{PO}_4)_2$ have been reported in the literature: $\text{Ba}_2\text{T}(\text{PO}_4)_2$ [$\text{T} = \text{Ni}$ (El Bali²), Cu (Etheredge³)]; $\text{BaT}_2(\text{PO}_4)_2$ [$\text{T} = \text{Co}$ (Bircsak⁴), Ni (El Bali⁵), Cu (Moqine⁶), Zn (Schmidt⁷)]; $\text{Sr}_2\text{T}(\text{PO}_4)_2$ [$\text{T} = \text{Ni}$ (El Bali⁸)]; $\text{SrT}_2(\text{PO}_4)_2$ [$\text{T} = \text{Co}$ (El Bali⁹), Ni (El Bali¹⁰), Zn (Hemon¹¹)]. During our investigation of the "binary" system: $\text{Sr}_3(\text{PO}_4)_2\text{-Ni}_3(\text{PO}_4)_2$ (El Bali¹²), we pointed out the evolution of the nickel-oxygen framework dimensionality in some of these mixed orthophosphates. Thus, analysis of the crystal structures of orthophosphates in this system shows a decrease of this dimensionality, from 3D in $\text{Ni}_3(\text{PO}_4)_2$ (Calvo¹³) and $\text{Sr}_2\text{Ni}(\text{PO}_4)_2$ (El Bali⁸) to 2D (Plane) in $\text{SrNi}_2(\text{PO}_4)_2$ (El Bali¹⁰). The linear link of Ni^{+2} , and even the isolated ones, characterise respectively the structures of $\text{SrNi}_3(\text{P}_2\text{O}_7)_2$ and SrNiP_2O_7 (El Bali¹). A similar decrease in the connectivity of nickel-oxygen coordination polyhedra is observed in quaternary diphosphates in the system $\text{Sr}_2\text{P}_2\text{O}_7\text{-Ni}_2\text{P}_2\text{O}_7$. $\text{Ni}_2\text{P}_2\text{O}_7$ in its α -, β - and σ -form shows a 2D network (Lukaczewicz¹⁴, Pietraszko¹⁵, Masse¹⁶). The connectivity of the nickel-oxygen polyhedra is not affected by the "substitution" of Sr by Ba (El Bali¹⁷). It decreases however rapidly when substituting Ni by Zn. The present work deals with the crystal structure of the new Nickel-Zinc Orthophosphate $\text{SrNiZn}(\text{PO}_4)_2$, which is isostructural to $\text{SrNi}_2(\text{PO}_4)_2$.

EXPERIMENTAL

Stoichiometric amounts of SrCO_3 , NiO , ZnO and $(\text{NH}_4)_2\text{HPO}_4$, compatible with the chemical formula $\text{SrNiZn}(\text{PO}_4)_2$, were dissolved in dilute nitric acid. After evaporating water, the residue was dried on a heating-stirrer and heated, in a tubular furnace, at higher temperatures (6h at 873 K, 24h at 1173K). Finally, a yellowish single phase powder has been obtained. This powder has been melted at 1523 K and subsequently cooled down, at a rate of 10°/h, to 873K. From the solidified melt red crystals of $\text{SrNiZn}(\text{PO}_4)_2$ were isolated. Crystal data, experimental

conditions for X-ray diffraction, data collection and structure refinement results are reported in Table 1.

Table 1: Crystal data, experimental conditions for X-ray diffraction, data collection, structure refinement results

I-Crystal data		II- Intensities measurements	
Formula	SrNiZn(PO ₄) ₂	Temperature [K]	293(2)
Crystal system	Triclinic	λ [Mo(K α)]	0.71073 Å
S. G	P-1 (N° 2)	[θ] (°)	2.45 – 24.97
Parameters (Å, °)	a = 5.456 (1)	Abs. Correct.	empirical / psi-scan
	b = 6.711 (1)	n-zero reflexions	1009
	c = 9.182 (1)	observed	1114
	α = 110.60 (1)	h_{\min} - h_{\max}	-6 – 6
	β = 101.10 (1)	k_{\min} - k_{\max}	-7 – 7
	γ = 98.08 (1)	l_{\min} - l_{\max}	-10 – 0
V(Å ³), Z	300.77(8), 2	III- Refinement	
d_{cal} (g/cm ³)	4.392	used programme	SHELX-97 package (Sheldrick ¹⁸)
Color	red	Indep. Parameters	119
F(000)	376	Agreement factors:	
		R ₁ /wR ₂ (%)	6.98 / 7.03
		R _{all}	2.75

RESULTS AND DISCUSSION

The framework of SrNiZn(PO₄)₂ contains isolated [PO₄]⁻³ groups. Their average \bar{d} (P-O) distance of 1.541(4) Å could be considered as identical to 1.542 Å in SrNi₂(PO₄)₂ (El Bali¹⁰). The cations Ni⁺² show sixfold coordination [NiO₆], with average \bar{d} (Ni-O) of 2.078 Å, which is close to the value 2.072 Å in SrNi₂(PO₄)₂. In fact, in this later structure, Ni⁺² occupy two kind of Ni coordination: [Ni(1)O₆] and [Ni(2)O₅₊₁]. Comparing the two crystal structures, we conclude that Zn⁺² ion sites in the position of Ni(1) with a reduction of its coordination number to 5 which results in a small contraction: ($V_{\text{SrNiZn}}/V_{\text{SrNi}_2} = 1\%$). Average $d_{\text{Zn-O}}$, 2.090 Å, is shorter than 2.144 Å in this site in SrNi₂(PO₄)₂. Edge-sharing of [NiO₆] and [ZnO₅] leads to sheets [NiZnO₉]_{2∞} as shown of Figure 1, drawn according to the data reported in Tables 2 and 3. The structure shows big similarity with that of SrNi₂(PO₄)₂, however here Ni form dimers [Ni₂O₁₀] in which the short distance $d_{\text{Ni-Ni}}$ is equal to 3.006 Å, as in SrNi₂(PO₄)₂ (2.993 Å). Figure 2 shows the oxygen coordination polyhedra of Ni⁺² and Zn⁺² in SrNiZn(PO₄)₂. The 3D network extension in SrNiZn(PO₄)₂ is ensured by Sr-O interactions from Sr⁺² ions located in octacoordinated sites. The mean value of (Sr-O) = 2.643 Å, is comparable to the homologous bond in SrNi₂(PO₄)₂, which is equal to 2.641 Å. For the visualisation of the evolution of the Ni dimensionality in the systems Sr₃(PO₄)₂-Ni₃(PO₄)₂ and Sr₂P₂O₇-Ni₂P₂O₇, we report on figure 3a-d projections of the crystal structures of the isolated compounds in these systems, ie: Sr₂Ni(PO₄)₂, SrNi₂(PO₄)₂, SrNiP₂O₇ and SrNi₃(P₂O₇)₂.

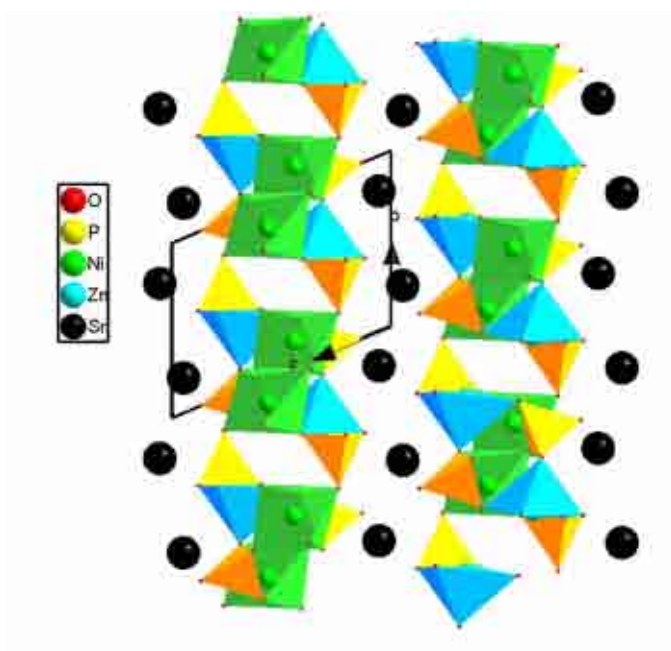


Figure 1: Perspective view of the crystal structure of $\text{SrNiZn}(\text{PO}_4)_2$ [Diamond¹⁹, 1999]
 Polyedra: Yellow (PO_4), Green (NiO_6), Light-blue (ZnO_5); Black balls: Sr^{+2}

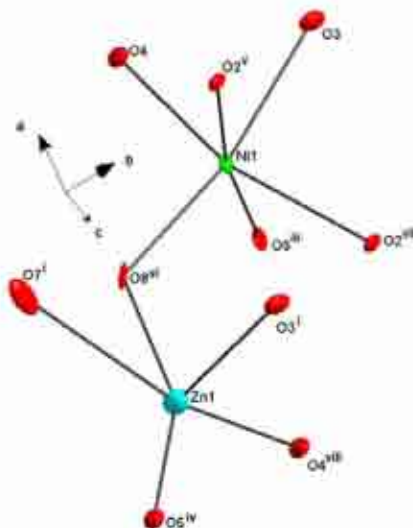


Figure 2: $\text{SrNiZn}(\text{PO}_4)_2$: View of the Ni and Zn coordination polyhedra. Displacement ellipsoids are at 60% level (Symmetry operators for generating equivalent atoms as in Table 3)

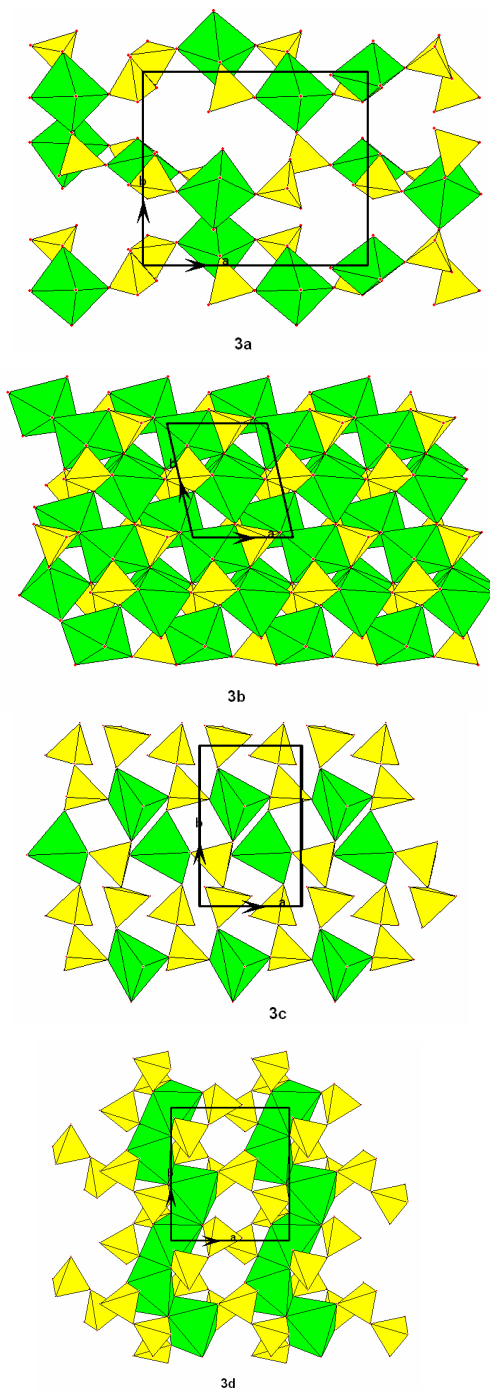


Figure 3: Ni distribution in four structures determined in the systems $\text{Sr}_3(\text{PO}_4)_2\text{-Ni}_3(\text{PO}_4)_2$ and $\text{Sr}_2\text{P}_2\text{O}_7\text{-Ni}_2\text{P}_2\text{O}_7$: $\text{Sr}_2\text{Ni}(\text{PO}_4)_2$ (a), $\text{SrNi}_2(\text{PO}_4)_2$ (b), SrNiP_2O_7 (c) and $\text{SrNi}_3(\text{P}_2\text{O}_7)_2$ (d)

Table 2: Atomic coordinates and isotropic displacement parameters for SrNiZn(PO₄)₂ (Esd's are given in parentheses)

Atom	x	y	z	U _{eq}
Sr	0.25316(9)	0.79867(7)	0.05416(5)	0.00612
Ni	0.36057(12)	1.14552(10)	0.44015(7)	0.0037
Zn	-0.00755(12)	0.40345(10)	-0.34850(8)	0.0084
P(1)	-0.1556(2)	1.0256(2)	0.30319(15)	0.0038
P(2)	0.3948(2)	0.42803(19)	0.23976(15)	0.0034
O(1)	-0.2525(7)	0.9992(6)	0.1310(4)	0.0081
O(2)	-0.3788(6)	0.9540(5)	0.3683(4)	0.0054
O(3)	0.0474(6)	0.8851(6)	0.3123(4)	0.0073
O(4)	-0.0043(7)	1.2636(6)	0.4180(4)	0.0080
O(5)	0.3461(7)	0.1970(5)	0.2367(4)	0.0061
O(6)	0.6537(7)	0.4840(6)	0.2043(4)	0.0073
O(7)	0.1712(7)	0.4520(6)	0.1211(5)	0.0113
O(8)	0.3795(6)	0.5933(5)	0.4041(4)	0.0062

a)
$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

Table 3: SrNiZn(PO₄)₂, interatomic distances in Ni, P and Zn polyhedra

Ni- O(8) ^{vi} : 1.971(4)	Zn- O(6) ^{iv} : 1.988(4)
Ni- O(5) ⁱⁱⁱ : 2.005(3)	Zn- O(8) ⁱ : 2.000(3)
N- O(3): 2.073(4)	Zn- O(4) ^{viii} : 2.020(4)
Ni- O(2) ⁱⁱⁱ : 2.080(3)	Zn- O(3) ⁱ : 2.066(3)
Ni- O(2) ^v : 2.095(3)	Zn- O(7) ⁱ : 2.374(4)
Ni- O(4): 2.244(4)	<Ni-O> = ; <Zn-O> =
Sr- O(1) =	<Sr-O> =
P(1)- O(1): 1.505(4)	P(2)- O(5): 1.525(3)
P(1)- O(2): 1.546(3)	P(2)- O(6): 1.535(3)
P(1)- O(3): 1.561(3)	P(2)- O(7): 1.539(4)
P(1)- O(4): 1.566(4)	P(2)- O(8): 1.553(3)
<P-O>	

Symmetry codes:

- (i) -x, 1-y, -z; (ii) -x, 2-y, -z; (iii) x, 1+y, z; (iv) 1-x, 1-y, -z;
 (v) 1+x, y, z; (vi) 1-x, 2-y, 1-z; (vii) -x, 2-y, 1-z; (viii) x, -1+y, -1+z;
 (ix) -1+x, y, z; (x) x, 1+y, 1+z; (xi) x, -1+y, z.

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