EVOLUTION OF NICKEL-OXYGEN FRAMEWORK'S DIMENSIONALITY IN SOME NICKEL(II)-ORTHOPHOSPHATES

BRAHIM EL BALI⁽¹⁾, ALI BOUKHARI⁽²⁾ AND HASSAN ALLOUCHI⁽³⁾

⁽¹⁾ University Sidi Mohammed ben Abdellah, Faculty of Sciences "Dhar Mehraz", BP 1796 Fès-Atlas, Department of Chemistry,

Fès, Morocco.

⁽²⁾ University Mohammed V, Faculty of Sciences, Laboratoire de Chimie du Solide Appliquée, Av. Ibn Batouta,

Rabat, Morocco.

⁽³⁾ Université de Tours, Laboratoire de Chimie Physique - PIMIR E. A. 2098, Faculté de Pharmacie, 31, Avenue Monge

37200 Tours, France.

Abstract : $\text{SrNiZn(PO}_4)_2$ is isostructural to $\text{SrNi}_2(\text{PO}_4)_2$ [P-1, Z=2, $a = 5.4560(10)$, $b = 6.7110(10)$, $c = 9.1820(10)$, $\alpha = 110.600(10)$, $\beta = 101.100(10)$, $\gamma = 98.080(10)$, 1009 independent reflexions ($I > 2\sigma(I)$), 119 parameters, $R1 = 6.98$, $wR = 7.03$], with sheets made of edge-sharing $[\text{NiO}_6]$ and $[\text{ZnO}_5]$. However in the new compound, Ni form 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 $\text{T}_3(\text{PO}_4)_2$ (M = Alkaline-Earth, T = 3d-transition metal) have been studied for a long time in some detail (El Bali¹ and references therein). During the last decades following mixed orthophosphates $\text{M}_{3-x}\text{T}_x(\text{PO}_4)_2$ have been reported in the literature: $\text{Ba}_2\text{T}(\text{PO}_4)_2$ [T = Ni (El Bali²), Cu (Etheredge³)]; $\text{BaT}_2(\text{PO}_4)_2$ [T = Co (Bircsak⁴), Ni (El Bali⁵), Cu (Moquine⁶), Zn (Schmidt⁷)]; $\text{Sr}_2\text{T}(\text{PO}_4)_2$ [T = Ni (El Bali⁸)]; $\text{SrT}_2(\text{PO}_4)_2$ [T = Co (El Bali⁹), Ni (El Bali¹⁰), Zn (Hemon¹¹)]. In our investigation of the "binary" system: $\text{Sr}_3(\text{PO}_4)_2\text{-Ni}_3(\text{PO}_4)_2$, which was the topic of our thesis work (El Bali¹²), we pointed out the evolution of the nickel-oxygen framework's 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 enchainment of Ni^{+2} , and even the isolated ones, characterize 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

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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 SrCO_3 , NiO , ZnO and $(\text{NH}_4)_2\text{HPO}_4$, according to the chemical formula $\text{SrNiZn}(\text{PO}_4)_2$, were dissolved in dilute nitric acid. After evaporating water and nitric acid 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 $10^\circ/\text{h}$, to 873K. From the solidified melt red crystals of $\text{SrNiZn}(\text{PO}_4)_2$ were isolated.

Discussion

The framework of $\text{SrNiZn}(\text{PO}_4)_2$ contains isolated $[\text{PO}_4]^{-3}$ groups. Their average $\bar{d}(\text{P-O})$ distance of 1.541(4) Å is to compare to 1.542 Å in $\text{SrNi}_2(\text{PO}_4)_2$ (El Bali¹⁰). Ni^{+2} shows sixfold coordination $[\text{NiO}_6]$, with average $\bar{d}(\text{Ni-O})$ of 2.078 Å, which is close to the value 2.072 Å in $\text{SrNi}_2(\text{PO}_4)_2$. In fact, in this later structure, Ni^{+2} occupy two kind of Ni coordination: $[\text{Ni}(1)\text{O}_6]$ and $[\text{Ni}(2)\text{O}_{5+1}]$. Comparing the two crystal structures, we conclude that Zn^{+2} ions site in the position of Ni(1) with a reduction of its coordinence to 5 which result 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 $\text{SrNi}_2(\text{PO}_4)_2$. Edge-sharing of $[\text{NiO}_6]$ and $[\text{ZnO}_5]$ leads to sheets $[\text{NiZnO}_9]_{2\infty}$ (Fig. 1). The new structure shows big similarity with that of $\text{SrNi}_2(\text{PO}_4)_2$, however here Ni form dimers $[\text{Ni}_2\text{O}_{10}]$ in which the short distance $d_{\text{Ni-Ni}}$ is of 3.006 Å, nearby same as in $\text{SrNi}_2(\text{PO}_4)_2$ (2.993 Å). We report on Fig. 2 the oxygenated coordination polyhedra of Ni^{+2} and Zn^{+2} in $\text{SrNiZn}(\text{PO}_4)_2$. The 3D network extension in $\text{SrNiZn}(\text{PO}_4)_2$ is ensured by Sr-O interactions from Sr^{+2} ions located in octacoordinated sites. Average $\bar{d}(\text{Sr-O})$, of 2.643 Å is to compare to its homologous in $\text{SrNi}_2(\text{PO}_4)_2$, 2.641 Å.

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 $\bar{1}$	[θ] (°)	2.45 – 24.97
Parameters (Å, °)	a = 5.4560(10)	Abs. Correct.	empirical / psi-scan
	b = 6.7110(10)	n-zero reflexions	1009
	c = 9.1820(10)	observed	1114
	α = 110.600(10)	$h_{\min}$ - $h_{\max}$	-6 – 6
	β = 101.100(10)	$k_{\min}$ - $k_{\max}$	-7 – 7
V(Å ³), Z	γ = 98.080(10)	$l_{\min}$ - $l_{\max}$	-10 – 0
	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	
Nbre parameters	119	factors: R_1/wR_2	6.98 / 7.03
		R_{all}	2.75

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) $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} \mathbf{a}_i^* \cdot \mathbf{a}_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

TABLE 3 $\text{SrNiZn}(\text{PO}_4)_2$, Interatomic distances in Ni, P and Zn polyedra.

Ni- O(8) _(2_121) : 1.971(4)	Zn- O(6) _(2_110) : 1.988(4)
Ni- O(5) _(1_010) : 2.005(3)	Zn- O(8) _(2_010) : 2.000(3)
N- O(3) : 2.073(4)	Zn- O(4) _(1_0-1-1) : 2.020(4)
Ni- O(2) _(2_021) : 2.080(3)	Zn- O(3) _(2_010) : 2.066(3)
Ni- O(2) _(1_100) : 2.095(3)	Zn- O(7) _(2_010) : 2.374(4)
Ni- O(4) : 2.244(4)	
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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)

Symmetry code: 1: (1, 1, 1), 2: (-1, -1, -1).

O(n)_{m-pqr}: translated "t(p, q, r)" symmetrical "m"- nth Oxygen.

FIGURE 1. Crystal structure of $\text{SrNiZn}(\text{PO}_4)_2$, projection along [100].

FIGURE 2. View of the Ni and Zn coordination polyhedra in $\text{SrNiZn}(\text{PO}_4)_2$, Ellipoids are shown at 50% probability level.

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