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Synthesis and structure of a porous zinc vanadate, $Zn_3(VO_4)_2\cdot 3H_2O$

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A zinc vanadate with the formula $Zn_3(VO_4)_2\cdot 3H_2O$ was synthesized by hydrothermal reaction of a gel of composition $[(CH_3CO_2)_2Zn\cdot 2H_2O] : 0.5V_2O_5 : 0.4$ [1,3-diaminepropane] : 1.5 NaOH : 114 H_2O, held at 170°C for 24 hours. The structure was determined ab initio by means of the EXPO direct methods program and refined with GSAS. The pale yellow solid crystallizes in the hexagonal space group P-6 with $a = 6.07877(8)$, $c = 7.1827(2)$ Å. The structure consists of vanadium tetrahedra bonded to distorted octahedral zinc atoms to create one dimensional columnar passageways for molecules. Though occupied by water in the as synthesized form, the passages could host other small molecules.

1. Introduction

The past half century has witnessed an important progression in new molecular sieve materials: aluminosilicate zeolites of the most diverse architecture, pore dimensions and applicability [1]; neutral aluminophosphate micro porous solids of zeolitic and of new and even predicted geometry [2]; metal substituted aluminophosphates of novel catalytic applicability [3]; and ultimately larger pore materials of structurally ordered nature [4, 5]. A continuation of this abundance of new compositions and geometries, all related by the essential presence of at least one member of the triad Si^{4+}, Al^{3+}, P^{5+}, or their periodic table analogs, is to be expected.

On the other hand, progress has been slow toward the preparation of micro porous solids containing transition metal elements with one or none of the components of the triad, even though the metals posses the qualities necessary to act as building blocks in such crystalline geometries. Worth mentioning are a few like the molybdenum phosphate, titanium silicate and zirconium arsenate systems [6], aside from the zinc phosphates, of course, which deserve a place apart [7]. As compared to the Si^{4+}, Al^{3+}, P^{5+} defined crystals, the transition metal containing substances could provide unsuspected vitality to catalysis and the science of materials.

Systems containing vanadium are of particular interest because of the rich structural chemistry of that element which easily adapts to tetrahedral, square pyramidal, and octahedral coordination environments, in various oxidation states, from which colorful catalytic properties might be expected. In this paper we report the synthesis and structure of a porous zinc vanadate compound with composition $Zn_3(VO_4)_2\cdot 3H_2O$.

2. Experimental

2.1. Materials and methods

The zinc vanadate was synthesized using $(CH_3COO)_2Zn\cdot 2H_2O$ (MERCK) as the zinc source and V_2O_5 (MERCK) as the vanadium source; 1,3-diaminepropane (SIGMA) and NaOH (Analyticals), as intended template and mineralizing agent, respectively, without further purification.

Thermo gravimetric analysis was carried out on a TA Instruments Hi-Res 2950 unit at a heating rate of 20°C/min under a nitrogen atmosphere. Tests of differential scanning calorimetry were similarly done on a TA Instruments DSC 2920. The zinc and vanadium contents in the solid were determined using a Perkin Elmer 2380 equipment, after dissolving an amount of sample in HCl aqueous solution. The powder X-ray diffraction pattern was obtained on a STOE STADIP diffractometer, fitted with a curved germanium (111) primary monochromator and a linear position sensitive detector. Cu $K_{\alpha}1$ radiation was used from a source operating at 40 kV and 40 mA. The data set was collected using a Debye Scherrer geometry (capillary tube, diameter 0.3 mm), at room temperature, from 7 to 90° in 2θ, step size of 0.02° and a count time of 8.7 s/step.

2.2. Synthesis

To 30 ml of H_2O was added 1.53 g of NaOH followed by 2.27 g of V_2O_5 which, on stirring, produced a lightly yellow clear solution; then 0.82 ml of 1,3-diaminepropane was added drop wise and finally a solution prepared with 5.49 g of $(CH_3COO)_2Zn\cdot 2H_2O$ in 21 ml of H_2O. The gel thus obtained was homogenized for two hours and then transferred to a Teflon lined stainless steel autoclave, sealed and heated at 170°C

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for 24 hours. The solid obtained was filtered, washed with water and dried a 100°C.

2.3. Characterization

A comparison of the X-ray powder diffraction pattern of the solid proved to be unique and different from all the other compositionally related species found in the open literature. From atomic absorption analysis, however, a Zn/V ratio of $\cong 1.4$ allowed to establish the composition of $Zn_3V_2O_8$ and brought the material close to that reported by Gopal *et al.* [8]. These authors give an account of the structure of α-$Zn_3(VO_4)_2$, solved by single crystal methods; the product, synthesized from the melt, crystallizes in the orthorhombic space group *Cmca* with $a = 6.088$, $b = 11.489$, and $c = 8.280$ Å and $Z = 4$. Further analysis revealed additional conclusive differences.

Fig. 1 shows the thermal behavior of the vanadate. The observed weight loss of ca. 12% up to 400°C, together with the bulk chemical analysis mentioned above, suggest the condensed formula $Zn_3(VO_4)_2 \cdot 3H_2O$ (F.W. = 479.99; water content 11.25%). The large endothermic peak corresponds to water evolution in one single slow event spanning about 200°C. No evidence of amine incorporation was found.

On the other hand, from the x-ray data, a set of 39 reflections whose $2\,\theta$ values were automatically produced by FULLPROF [9], subject to default parameters and individual inspection, were used as input to the program TREOR90 [10]. The best solution, showing a figure of merit of 192, belonged to the hexagonal system with $a = 6.051$ and $c = 7.195$ Å. No systematically absent reflections were evident in the powder pattern, allowing the tentative assignment of P-6 as the space group.

3. Solution and description of the structure

The composition $Zn_3V_2O_{11}$ was initially given as input to the program EXPO[11], with the rest of the variables in default values. The calculated E-map showed the atomic positions shown in Table I, with a figure of merit of 0.992 and a residual $R = 8.84\%$. These coordinates were then used as a model for the GSAS[12] refinement program.

TABLE I EXPO coordinates

Atom	Height	X	Y	Z	Occ.
Zn	1721	0.346	0.156	0.000	0.500
V	1076	0.333	0.667	0.750	0.333
o1	278	0.193	−0.172	0.814	1.000
o2	360	0.000	0.000	0.500	0.167
o3	373	0.667	0.333	0.139	0.333
o4	205	0.333	0.667	0.500	0.167

Notice that, according to Table I, the condensed formula would be $Zn_3V_2O_{10}$ and there is one oxygen atom missing to explain the TGA results.

Constant wavelength profile function #3 with 19 coefficients and a 15-term Cosine Fourier series background function #2, of the GSAS [12] Rieltveld program, were used in the refinement, with a damping factor of 5. Before allowing the atomic positions to adjust, soft constraints were placed as follows: V–O 1.7; Zn–O 2.0 and 2.3 (to take into account the longest bond); initial weighting factor $F = 3000$.

In the final stages of refinement, difference Fourier maps showed a positive residual electron density around oxygen O_2. But notice that this atom corresponds to water located in the structure channels at Wyckoff position b of symmetry −6 and multiplicity 1. Since the oxygen atoms found so far did not explain the TGA results, it was postulated that the true location of the water molecules might be Wyckoff position g of symmetry 3 and multiplicity 2. Refinement of the fraction of O_2 improved the agreement R factors significantly. The refined occupancy of the water oxygen then brought the total oxygen contents in conformity with the thermal analysis. Water then occupies a site of lower symmetry to accommodate a larger population.

The last cycles of refinement were done with $F = 500$ and produced the final agreement factors $Rp = 0.0567$, $wRp = 0.0748$, $R(F^2) = 0.0831$. Table II provides

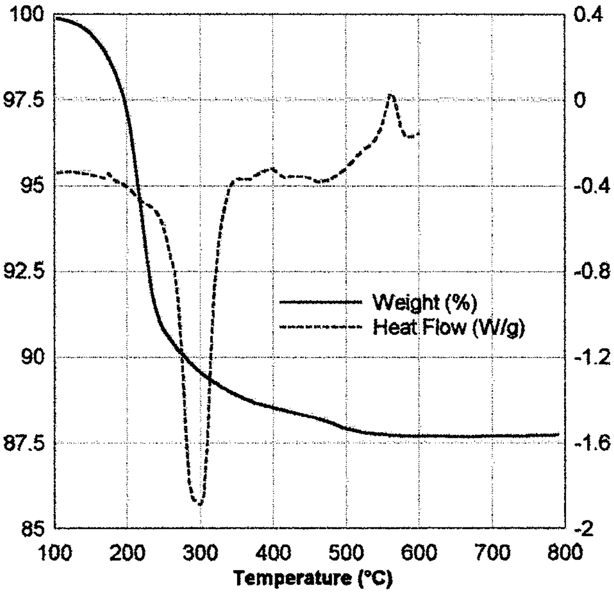

Figure 1 TGA and DSC curves for $Zn_3(VO_4)_2 \cdot 3H_2O$.

TABLE II Final coordinates, thermal factors and multiplicities

Name	X	Y	Z	Ui/Ue*100	Site sym	Mult	Fractn
Zn	0.3301(8)	0.1575(9)	0.000	1.49(7)	M(001)	3	1.0
V	1/3	2/3	0.7542(4)	1.31(10)	3	2	1.0
o1	0.1452(14)	−0.2141(11)	0.8241(7)	2.0(2)	1	6	1.0
o2	0.000	0.000	1/2	2.0(2)	3	2	1.93(3)
o3	2/3	1/3	0.1257(13)	2.0(2)	3	2	1.0
o4	1/3	2/3	1/2	2.0(2)	−6	1	1.0

details of the final coordinates and additional parameters of the asymmetric unit shown in Fig. 2, where two such units are detailed to explain the linkage between neighboring layers.

The observed and calculated profiles after the Rietveld refinement of $Zn_3(VO_4)_2{\cdot}3H_2O$ appear in Fig. 3, together with the difference plot (bottom).

Table III offers a selection of bond distances and angles. It also shows that the oxygen atom o1 is three-coordinated, to two Zn and one V atom, as was observed in α-$Zn_3(VO_4)_2$.

A view down the *c* axis of the structure (Fig. 4), shows a honeycomb pattern typical of hexagonal arrangements.

The zinc vanadate shares common features with other reported structures, like the zinc and nickel molybdates of Ying *et al.* [13, 14]. The lattice is formed by sheets of distorted zinc octahedra in rows running along the *a* axis (Fig. 5). The octahedral rows are linked through vanadate groups which extend two vertices to consecutive edge sharing octahedra in one row and a third vertex which serves as bridge to the adjacent row. The fourth tetrahedral vertex links to an opposite vertex in the contiguous layer.

Thus, there is an infinite stack of layers where the metal atoms in their different environments reside, and there are pillars holding the stacks together, to create molecular galleries much like the micro pores observed in zeolites. The apertures in zeolites, however, are delimited by stronger multi-chain formed "pillars", as opposed to the single chains observed here. Though occupied by water molecules in the as-synthesized

TABLE III Selected bond distances and angles

Distances (Å)			
zn-o1	2.329(7)	v-o1	1.707(6)
zn-o1	2.113(8)	v-o4	1.826(3)
zn-o3	1.989(5)		
Angles (°)			
o1-zn-o1	73.5(2)	o1-v-o1	111.8(2)
o1-zn-o3	120.3(5)	o1-v-o4	107.1(2)
o1-zn-o3	88.2(4)		
o3-zn-o3	54.0(2)		

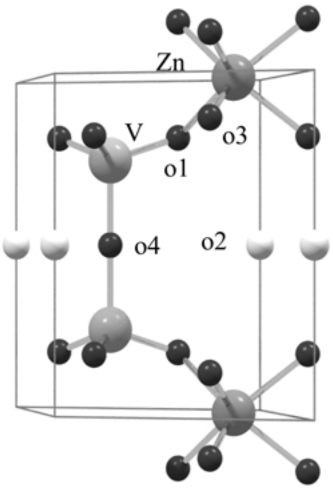

Figure 2 Asymmetric unit.

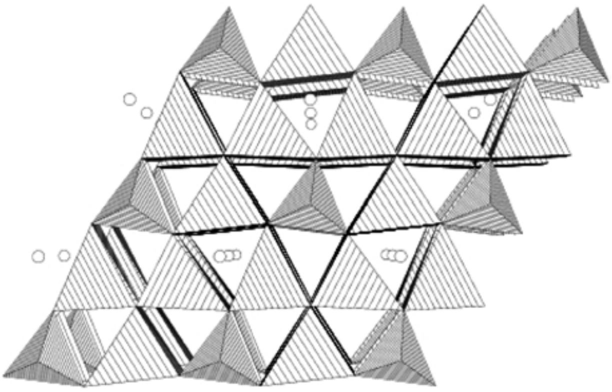

Figure 4 View of the zinc vanadate down the *c* axis.

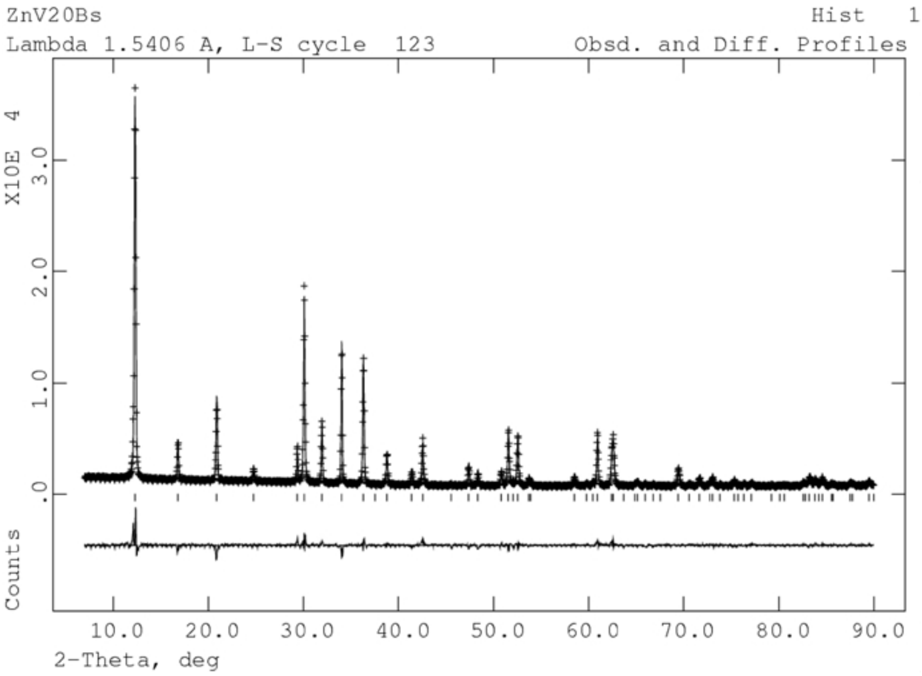

Figure 3 Observed (cross), calculated (line) and difference (bottom) profiles.

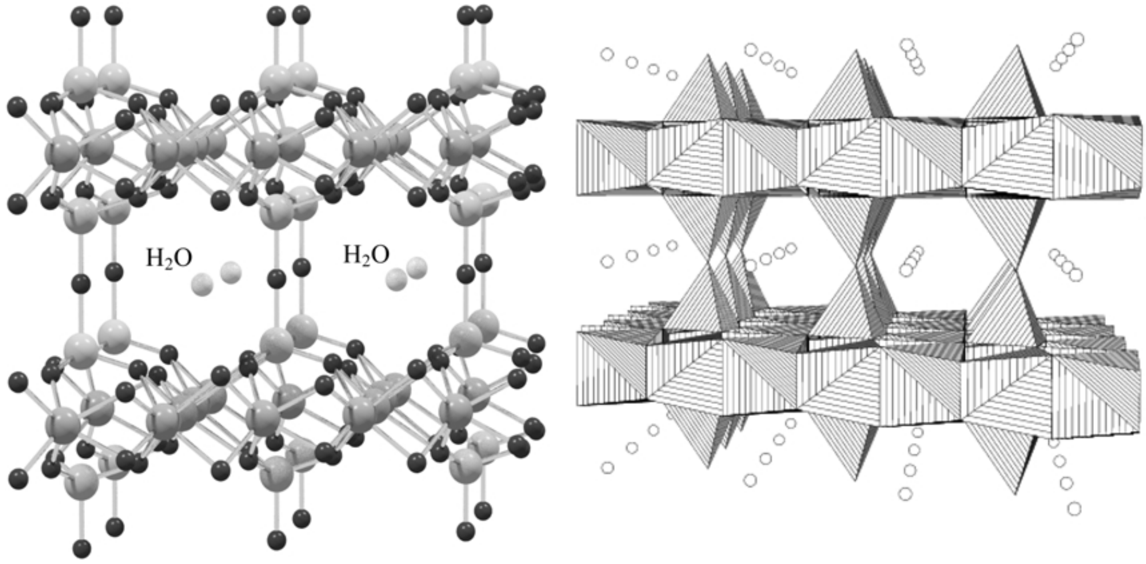

Figure 5 Ball and stick (left) and polyhedral view (right) of the structure along the *a* axis.

form, the molecular galleries in $Zn_3(VO_4)_2{\cdot}3H_2O$ could host other small molecules.

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