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Hydrothermal synthesis and characterization of a new aluminium vanadium oxide hydroxide $Al_2(OH)_3(VO_4)$

Brigitte Pecquenard, Peter Y. Zavalij and M. Stanley Whittingham*†

Chemistry Department and Material Research Center, State University of New York at Binghamton, Binghamton, NY13902-6000, USA

A new aluminium vanadium oxide hydroxide analog of the mineral augelite has been prepared by hydrothermal treatment of a 1:1:2.65 aqueous solution of V_2O_5, $Al(NO_3)_3·9H_2O$, and TMAOH at 200 °C for 5 days. X-Ray powder diffraction data show that this phase crystallizes with monoclinic symmetry with space group *C*2/*m*. The structure was solved by using direct methods and then full profile Rietveld refinement was carried out; it's cell parameters are: $a = 13.5634(2)$ Å, $b = 8.2267(2)$ Å, $c = 5.31232(9)$ Å and $\beta = 112.741(1)°$ in space group *C*2/*m*. The structure contains clusters of edge sharing AlO_6 octahedra and AlO_5 trigonal bipyramids. These clusters are joined together by VO_4 tetrahedra.

Introduction

In a constant search for new compounds which could be used as cathodic materials for advanced lithium batteries, we focussed our research on new metastable vanadium oxides. The structure of the oxide lattice and a possible addition of a second metal are critical to obtain lithium insertion and reversible reaction. Indeed, a recent study on a $Fe_{0.11}V_2O_{5.16}$ compound obtained by the sol–gel process has shown that the presence of iron(III) ions in the orthorhombic host lattice induced a real improvement of its electrochemical properties compared to V_2O_5.[1] The use of '*chimie douce*' allows us to obtain new materials which are sometimes impossible to be formed by using solid state reactions at high temperature. Among these, the hydrothermal approach under mild conditions, using organic templates such as tetramethylammonium ion was found to be particularly adept at forming new structures.[2–17] It is noticeable that the template is often retained in the structure, as for $TMA_{0.17}V_2O_5$, $TMAV_3O_7$,[18] $TMAV_4O_{10}$[5,9] or $TMAV_8O_{20}$.[19] Recently, a study achieved by Zhang *et al.*[17] indicate the possible synthesis of iron and zinc double vanadium oxides using TMA.

Here we report the synthesis of a new aluminium vanadium oxide analog of the mineral augelite $Al_2(PO_4)(OH)_3$[20] by using tetramethylammonium ion as a template.

Experimental

The title compound was prepared by hydrothermal treatment by mixing V_2O_5 and $Al(NO_3)_3·9H_2O$ powder from Johnson and Matthey with 25% tetramethylammonium hydroxide (TMAOH) aqueous solution from Alfa in a 1:1:2.65 molar ratio. Typically, 5 g of V_2O_5, 10.3 g of $Al(NO_3)_3·9H_2O$ and 26.5 g of TMAOH were mixed together and the initial pH of the resulting solution was 3.21. Then, the solution was transferred to a 125 ml Teflon-lined autoclave (Parr bomb), sealed and reacted hydrothermally for 5 days at 200 °C. At shorter and longer reaction times second phases were formed, the compositions of which have not yet been determined. The resulting light brown powder was filtered, washed with distilled water and dried in air. The pH of the solution after reaction was 6.32, higher than that of the initial mixture.

X-Ray powder diffraction was performed using Cu-Kα radiation ($\lambda = 1.5418$ Å) on a Scintag XDS2000 θ–θ diffractometer. The data were collected from 17° 2θ to 90° 2θ with 0.03° 2θ steps and 15 s per step. The TGA was obtained on a Perkin-Elmer model TGA 7, the FTIR on a Perkin-Elmer 1600 series, and the electron microprobe on a JEOL 8900.

Results and Discussion

The resulting powder has a light brown color. The electron microprobe picture (Fig. 1) shows that the morphology of this new compound is well formed spherical particles, with an average diameter close to 70 µm. It seems that these particles result from a germination/growth process, with a nucleation point at the center of each particle. The X-ray diffraction pattern indicates the presence of sharp lines. Thermal gravimetric analysis of the compound under nitrogen (Fig. 2) shows a total weight loss of about 13.1% appearing in one step essentially due to loss of OH groups. From TGA and X-ray data, the general formula of the compound was found to be $Al_2(OH)_3(VO_4)$, the tetramethylammonium not being incorporated in the structure. The infrared spectrum (Fig. 3) confirmed the absence of tetramethylammonium ion which is usually characterized by three bands at 945, 1386 and

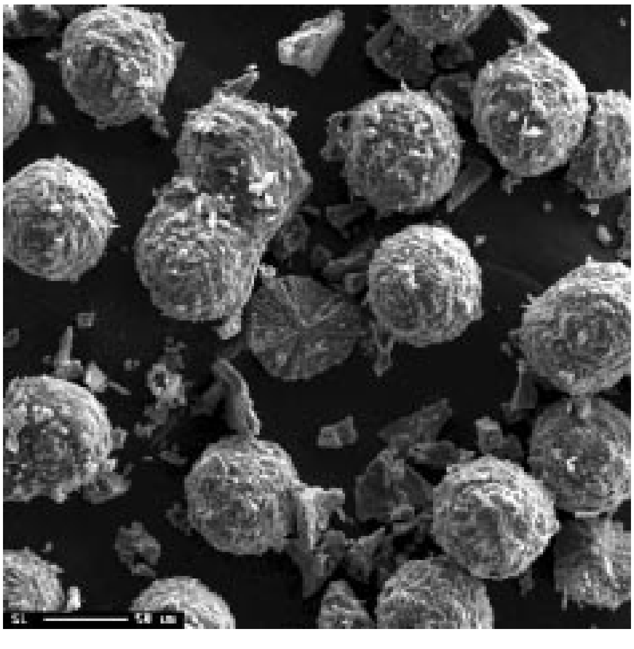

Fig. 1 Electron microprobe picture of $Al_2(OH)_3(VO_4)$

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†E-mail: stanwhit@binghamton.edu

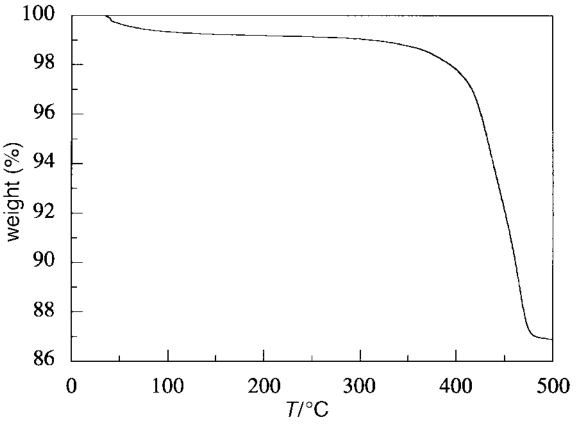

Fig. 2 Thermal gravimetric analysis of $Al_2(OH)_3(VO_4)$ under nitrogen

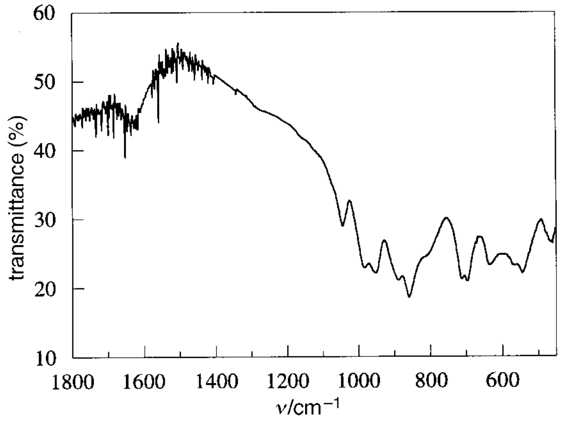

Fig. 3 Infrared spectrum of $Al_2(OH)_3(VO_4)$

1492 cm^{-1}.[21] All the bands are observed in the range 450–1050 cm^{-1} which correspond to the M—O bonds domain (M being a metallic atom). The precise assignment of IR peaks is however not obvious. Only characteristic frequency ranges are known for 'condensed' and 'isolated' Al—O octahedra and tetrahedra.[22] Peak positions are really dependent on the structure. After thermal treatment under air, the compound is decomposed into V_2O_5 and $AlVO_4$. The powder diffraction pattern was indexed with a monoclinic symmetry and the space group $C2/m$ using the Ito method from the CSD Software.[23] The cell parameters of this new compound are: $a = 13.5634(2)$ Å, $b = 8.2267(2)$ Å, $c = 5.31232(9)$ Å and $\beta = 112.741(1)°$. Integrated intensities of 87 peaks were used in direct methods to solve the structure. The powder X-ray diffraction patterns of the observed and calculated data after Rietveld refinement are shown in Fig. 4. The final refinement was achieved by using the CSD program and the results are collected in Table 1. This gave $R(F^2) = 0.062$ and R(profile) = 0.086. The calculated density of this new compound is 2.672 g cm^{-3}. The atomic positions, the selected interatomic distances and the bond angles are given in Tables 2 and 3.

The structure of this new aluminium vanadium hydroxide contains two types of polyhedra around aluminium (Fig. 5). Al(1) belongs to an octahedron with four OH groups and 2 O atoms. The cation–anion distances in the polyhedron vary from 1.821 Å to 1.995 Å with an average value of 1.896 Å. The other aluminium, Al(2), is surrounded by five neighbors: two O atoms and 1 OH group located in the basal plane and the other two OH groups quasi-perpendicular to this plane. The cation–anion distances in this trigonal bipyramid vary from 1.721 Å to 2.193 Å with an average value of 1.84 Å. 2 Al(1) and 2 Al(2) are bound together, sharing OH–OH edges. These aluminium clusters are connected to vanadium tetrahedra by sharing an oxygen apex (Fig. 6), which induces the existence of a continuous network. The projection of the structure along the b-axis (Fig. 7) shows that the groups of aluminium polyhedra are concentrated in layers parallel to the 00l plane, and separated by $d(001)$. It also highlights the existence of tunnels which contain hydrogen from the OH groups.

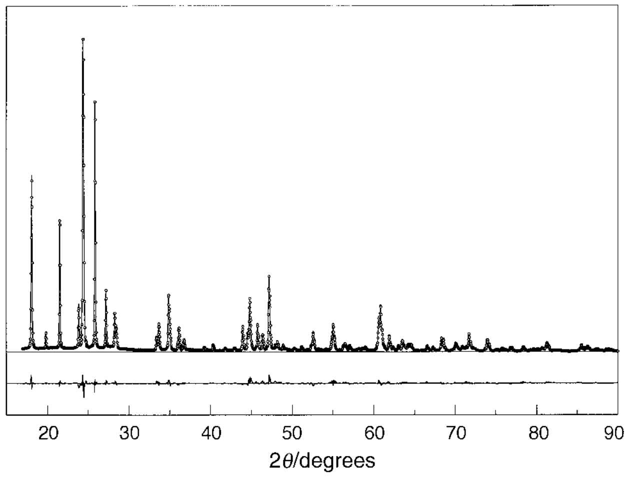

Fig. 4 Calculated X-ray diffraction pattern resulting from final Rietveld refinement (thin line), experimental data (dotted line) and a difference plot (on the bottom)

Table 1 Crystallographic data for $Al_2(OH)_3(VO_4)$

compound	$Al_2(OH)_3(VO_4)$
crystal system	monoclinic
space group	$C2/m$ (no. 12)
a/Å	13.5634(2)
b/Å	8.2267(2)
c/Å	5.31232(9)
β/°	112.741(1)
cell volume, V/Å^3	546.68(3)
calculated density, D_c/g cm^{-3}	2.672
absorption coefficient, μ/cm^{-1}	191.7
radiation, λ(Cu-Kα)/Å	1.54178
diffractometer	Scintag XDS2000
indexing method	Ito
software	CSD
mode of refinement	full profile
2θ (max)	90°
number of refined parameters	29 (21 atomic)
number of reflections	87
R(I)	0.062
R(prof)	0.086
R_w (prof)	0.105

Table 2 Atomic coordinates and thermal parameters for $Al_2(OH)_3(VO_4)$

atom	x/a	y/b	z/c	U_{iso}/Å	N
Al(1)	0	0.1911(5)	0.5	0.78(1)	4
Al(2)	0.1824(3)	0	0.4637(8)	1.01(1)	4
V	0.3510(2)	0	0.1210(5)	0.88(6)	4
O(1)	0.2463(7)	0	0.229(2)	1.438	4
O(2)	0.2962(6)	0	−0.242(2)	1.438	4
O(3)	0.4234(5)	0.1672(7)	0.233(1)	1.438	8
O(4)*	0.9171(6)	0	0.295(1)	1.438	4
O(5)*	0.1065(5)	0.1788(6)	0.358(1)	1.438	8

[a] O(4) and O(5) are bonded to hydrogen.

The structure is very close to that described for the mineral augelite $Al_2(OH)_3(PO_4)$. The cell parameters for the augelite structure are $a = 13.124$ Å, $b = 7.988$ Å, $c = 5.066$ Å and $\beta = 112.25°$.[20] The substitution of phosphorus by vanadium induces an increase of the cell parameters along the three directions. The array of the different polyhedra is similar, but the anion–cation distances in some polyhedra are slightly

Table 3 Selected interatomic distances and bond angles for $Al_2(OH)_3(VO_4)$

VO_4 tetrahedron	
V—O(1)	1.73(1)
V—O(2)	1.778(8)
V—O(3)	1.661(6)(×2)
O(1)—V—O(2)	108.0(4)
O(1)—V—O(3)	109.3(3)(×2)
O(2)—V—O(3)	109.2(3)(×2)
O(3)—V—O(3)	111.8(3)
Al(1) octahedron	
Al(1)—O(3)	1.821(6)(×2)
Al(1)—O(4)	1.995(6)(×2)
Al(1)—O(5)	1.873(7)(×2)
O(3)—Al(1)—O(3)	100.4(3)
O(3)—Al(1)—O(4)	92.7(3)(×2)
O(3)—Al(1)—O(5)	91.0(3)(×2)
O(3)—Al(1)—O(4)	164.3(3)(×2)
O(3)—Al(1)—O(5)	93.0(3)(×2)
O(4)—Al(1)—O(5)	95.5(3)(×2)
O(5)—Al(1)—O(5)	173.8(3)
Al(2) trigonal bipyramid	
Al(2)—O(1)	1.770(1)
Al(2)—O(2)	1.721(9)
Al(2)—O(4)	2.193(9)
Al(2)—O(5)	1.758(6)(×2)
O(1)—Al(2)—O(2)	97.3(4)
O(1)—Al(2)—O(5)	99.3(4)(×2)
O(2)—Al(2)—O(4)	90.4(3)
O(4)—Al(2)—O(5)	76.7(3)(×2)
O(5)—Al(2)—O(5)	113.6(3)
O(1)—Al(2)—O(4)	172.3(4)
O(2)—Al(2)—O(5)	119.9(4)(×2)

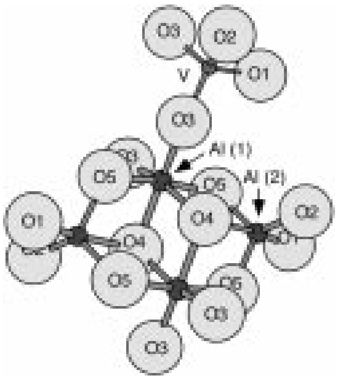

Fig. 5 Representation of an aluminium polyhedral group connected to a vanadium tetrahedron with the atom-labelling scheme. The aluminium polyhedral group is composed of two Al(1) octahedra and two Al(2) trigonal pyramids bound together by sharing OH–OH edges.

different. The Al(1) octahedron is quite similar with cation–anion distances which range from 1.826 Å to 1.983 Å and average 1.891 Å. The Al(2) trigonal bipyramid is less distorted in the augelite structure. In this case, the cation–anion distances range from 1.750 Å to 2.054 Å and average 1.833 Å which correspond to four short bonds, longer than in our compound, and a long bond, which is shorter than in our compound. The average distance in the phosphate tetrahedron is 1.519 Å compared with 1.706 Å for the vanadate, which induces a bigger unit cell, 546.7 $Å^3$ for the vanadate and 491.5 $Å^3$ for the phosphate.

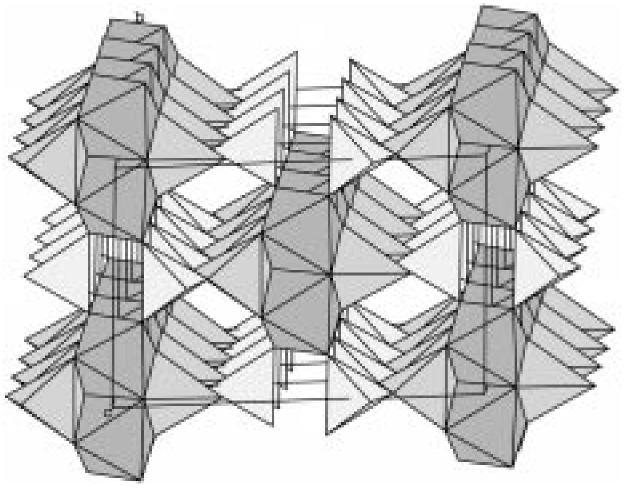

Fig. 6 Projection of the structure of $Al_2(OH)_3(VO_4)$ along the *c*-axis. Al(1), Al(2) and vanadium respectively occupy dark grey octahedra, medium grey trigonal pyramids and light grey tetrahedra.

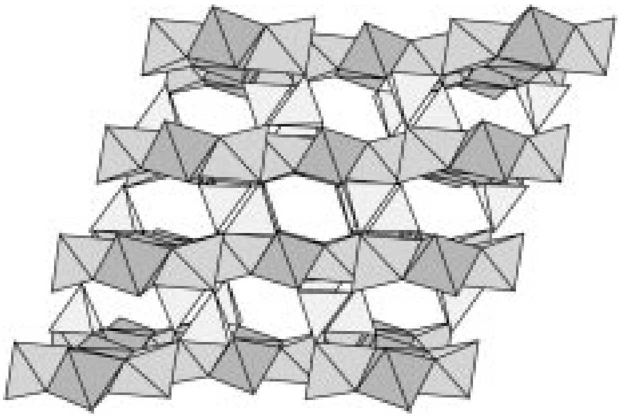

Fig. 7 Projection of the structure of $Al_2(OH)_3(VO_4)$ along the *b*-axis

Conclusion

Hydrothermal reactions occur naturally in the crust of the earth, aiding in the formation of minerals. They therefore might provide a viable route to synthesize materials under kinetic control which may exhibit new structures and properties.

A new aluminium vanadium oxide hydroxide $Al_2(OH)_3(VO_4)$ analog of the mineral augelite has been synthesized hydrothermally and structurally characterized. This was achieved by mixing vanadium pentoxide, aluminium nitrate and tetramethylammonium hydroxide. The last, used as a template, is not retained in the structure after reaction. This three dimensional structure is built up of clusters of aluminium octahedra and trigonal pyramids sharing edges. These clusters are connected together by vanadium tetrahedra. The structure of the mineral augelite $Al_2(OH)_3(PO_4)$, which is very similar, exhibits smaller cell parameters because of the shorter tetrahedral P—O bonds. Furthermore, this new compound as well as the mineral augelite is one of the few compounds to contain aluminium in a trigonal pyramidal environment. A study by ^{27}Al fast MAS NMR spectroscopy is now in progress.

There are numerous aluminium phosphate hydroxide structures, but $Al_2(OH)_3(VO_4)$ is the first related vanadate. There is just one other report of an aluminium vanadate hydroxide, but it is hydrated with the formula $Al_6V_{10}(OH)_{12}O_{28}{\cdot}29H_2O$, which indicates a decavanadate cluster.[24]

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