Synthesis and Structure of the Ternary Vanadate $NaMn_4(VO_4)_3$

Hamdi Ben Yahia[a,b], Etienne Gaudin[b], Ute Ch. Rodewald[a], and Rainer Pöttgen[a]

[a] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30, 48149 Münster, Germany
[b] ICMCB, CNRS, Université Bordeaux 1, 87 Avenue du Docteur Schweitzer, 33608 Pessac Cedex, France

Reprint requests to R. Pöttgen.
E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **2011**, *66b,* 437 – 440; received February 2, 2011

The vanadate $NaMn_4(VO_4)_3$ was obtained as dark-brown crystals as a side-product during the crystallization of the oxygen-deficient perovskite $Na_3MnV_2O_{7.5}$ in an NaCl/KCl flux. $NaMn_4(VO_4)_3$ crystallizes with the tetragonal $(Mg_{1/2}\square_{1/2})Mg_4(AsO_4)_3$ type, space group $I\bar{4}2d$. The structure was refined from single-crystal diffractometer data: a = 7.0238(2), c = 19.8360(9) Å, $R(F)$ = 0.013, $wR(F^2)$ = 0.033, 853 F^2 values, and 49 variables. The $NaMn_4(VO_4)_3$ structure is built up of different sheets stacked perpendicular to the c axis. Na, Mn and V atoms are located in dodecahedra, octahedra and tetrahedra, respectively.

Key words: Vanadates, Crystal Structure, MnO-V_2O_5-Na_2O Ternary System

Introduction

Many different structures have been observed for orthovanadates with the general composition $AB_4(VO_4)_3$ (A = Li, Na, K, and Rb, and B = Ca, Mg, and Cd). In the $ACd_4(VO_4)_3$ series, three different structure types are observed. The structure of $LiCd_4(VO_4)_3$ [1] is a modulated variant of the Na_2CrO_4 type [2], $NaCd_4(VO_4)_3$ crystallizes with the maricite structure [3], and compounds $ACd_4(VO_4)_3$ (A = K [4] and Rb [5]) adopt the scheelite structure. With increasing size of the A cation, its coordination number increases from 4 to 6 with associated structural changes. Moreover, disorder is often observed between the A and B cations. In the incommensurate structure of $LiCd_4(VO_4)_3$, or $(Li_{1/3}Cd_{1/3}\square_{1/3})CdVO_4$, the Li/Cd disorder induces strong steric strains in the tetrahedral sites and a strong modulation of their occupancies [1, 6]. In $NaCd_4(VO_4)_3$, or $(Na_{1/3}Cd_{1/3}\square_{1/3})CdVO_4$, an Na/Ca/vacancy disorder is observed in strongly distorted tetrahedral sites derived from an octahedral site [7]. In $KCd_4(VO_4)_3$ [4] and $RbCd_4(VO_4)_3$ [5], all sites are fully occupied, but slight Cd/alkali mixing is observed for some of these sites. For the $ACa_4(VO_4)_3$ series, only $NaCa_4(VO_4)_3$ has been reported [8], but without detailed structural data. Its structure has been recently determined [9] and was found to be isostructural with the mineral silicocarnotite, $Ca_5(PO_4)_2SiO_4$ [10]. The $NaCa_4(VO_4)_3$ structure is very similar to that of $Ca_3Y_2(SiO_4)_3$ [11] and $NaCd_4(PO_4)_3$ [12], with a silicocarnotite type. In the $AMg_4(VO_4)_3$ series, only $LiMg_4(VO_4)_3$ [13] and $NaMg_4(VO_4)_3$ [14] have been observed, and both crystallize with the same structure, different from that of the Cd analogs. No A/Mg disorder is observed in these structures; the Mg atoms occupy octahedral sites, and the alkali cations occupy sites with an eightfold coordination. For the $AMn_4(VO_4)_3$ series, to our knowledge, no compound has been reported in the literature. Herein we report on the successful synthesis and structure of $NaMn_4(VO_4)_3$ which is isotypic with $AMg_4(VO_4)_3$ (A = Li, Na) [13, 14].

Experimental Section

Synthesis

The title compound was first obtained as a by-product during the crystal growth attempts of $Na_3MnV_2O_{7.5}$ in a NaCl (Merck, > 99.5 %)/KCl (Chempur, > 99.9 %) (1:1 molar ratio) salt flux. $NaMn_4(VO_4)_3$ was then prepared by a solid-state reaction from a mixture of Na_2CO_3 (Aldrich, ≥ 99.5 %), MnO (Aldrich, > 99 %) and V_2O_5 (Merck, 99.99 %) with a 1 : 8 : 3 molar ratio. The mixture was put in a gold tube, which was placed in a silica tube and heated for a few minutes at ∼ 600 °C under dynamic vacuum in order to evacuate CO_2. Then it was sealed and fired at 500 °C for 24 h and at 650 °C for 100 h with intermediate grinding.

EDX data

Semiquantitative EDX analyses of many crystals including the one investigated on the diffractometer (Fig. 1) were carried out with a Leica 420i scanning electron microscope with albite (for Na), Mn and V as standards. The experimentally observed compositions were close to the composition obtained from the single-crystal refinement. Few crystals of compositions $NaMnVO_4$ and $Na_3MnV_2O_{7.5}$ were also observed.

0932–0776 / 11 / 0400–0437 $ 06.00

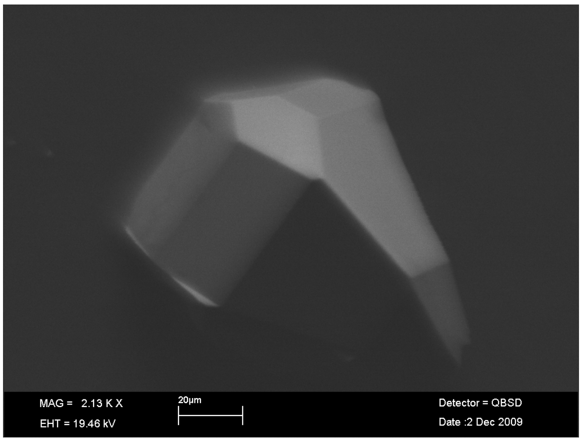

Fig. 1. SEM image of the $\mathrm{NaMn_4(VO_4)_3}$ single crystal used for the XR data collection.

X-Ray diffraction

At each reaction stage, the polycrystalline sample was characterized by a Guinier pattern (image plate system, Fujifilm BAS-1800) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 4.9130, c = 5.4046 Å) as an internal standard. This allowed us to confirm the purity of the phase (Fig. 2). The refined powder lattice parameters are: a = 7.0212(1) Å, b = 19.8327(9) Å and V = 977.70(6) Å^3.

A crystal suitable for single-crystal X-ray diffraction was selected on the basis of the size and the sharpness of the diffraction spots by Laue photographs on a Buerger camera (using white Mo radiation). The data collection was carried out on a Stoe IPDS II diffractometer using MoK_{α} radiation. Data processing and all refinements were performed with the JANA2006 program package [15]. A Gaussian-type absorption correction was applied, and the crystal shape was determined with the video microscope of the Stoe CCD diffractometer. Details about the data collection are summarized in Table 1.

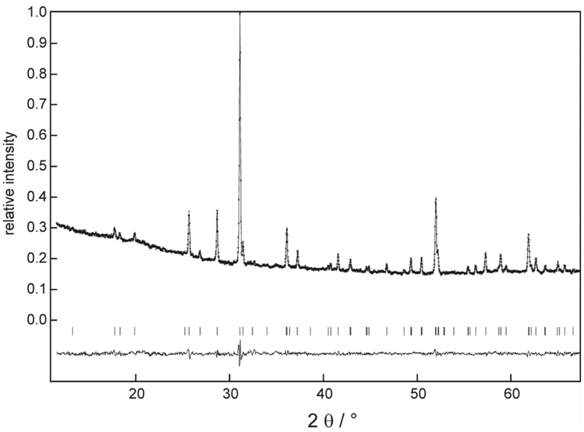

Fig. 2. Observed, calculated and difference plots for the XRPD profile refinement of the $\mathrm{NaMn_4(VO_4)_3}$ sample.

Table 1. Crystal data and structure refinement for $\mathrm{NaMn_4(VO_4)_3}$, space group $I\bar{4}2d$, Z = 4.

Refined composition	$\mathrm{NaMn_4(VO_4)_3}$
Formula weight, g mol^{-1}	587.6
Unit cell dimensions	
a, Å	7.0238(2)
c, Å	19.8360(9)
Cell volume, Å^3	978.6
Calculated density, g cm^{-3}	3.99
F(000), e	1104
Crystal size, μm^3	60 × 80 × 110
Transm. ratio (max / min)	0.694 / 0.526
Absorption coefficient, mm^{-1}	7.9
Detector distance, mm	80
Exposure time, min	3
ω range; increment, deg	0 – 180, 1.0
Integr. param. A, B, EMS	12.8; 3.3; 0.013
θ range for data collection, deg.	3.0 – 31.9
Range in hkl	±10, ±10, ±29
Total no. reflections	17176
Independent reflections / R_{int}	853 / 0.039
Data / ref. parameters	853 / 49
$R1$ / $wR2$ for all data	0.013 / 0.033
Extinction coefficient	2610(160)
Goodness-of-fit on F^2	0.88
Flack parameter x	0.01(2)
Largest diff. peak / hole, e Å^{-3}	0.21 / −0.21

Table 2. Coumpounds showing the same crystal structure (space group $I\bar{4}2d$, Z = 4).

Compounds	a (Å)	c (Å)	V (Å^3)	Ref.
$\mathrm{NaMn_4(VO_4)_3}$	7.024	19.836	978.6	this work
$\mathrm{NaMg_4(VO_4)_3}$	6.890	19.292	915.8	[14]
$\mathrm{NaMg_4(AsO_4)_3}$	6.817	19.242	894.2	[17]
$\mathrm{LiMg_4(VO_4)_3}$	6.867	18.954	893.8	[13]
$\mathrm{Co_{1/2}\square_{1/2}Co_4(AsO_4)_3}$	6.858	18.872	887.6	[18]
$\mathrm{Mg_{1/2}\square_{1/2}Mg_4(AsO_4)_3}$	6.783	18.963	872.5	[19]
$\mathrm{Fe_5(Fe_{0.17}Ge_{0.83})_2GeO_{12}}$	6.854	18.747	880.7	[20]
$\mathrm{Mg_{2.65}Fe_{0.49}Al_{1.95}Si_{2.91}O_{12}}$	6.527	18.183	774.6	[21]
$\mathrm{Ni_{4.35}As_3O_{11.7}(OH)_{0.3}}$	6.781	18.835	866.1	[22]

Structure refinement

The extinction conditions observed for $\mathrm{NaMn_4(VO_4)_3}$ were compatible with space group $I\bar{4}2d$. Most of the atom positions were located using the SUPERFLIP program [16]. The use of difference-Fourier syntheses allowed us to localize the remaing oxygen atom positions. With anisotropic displacement parameters for all positions, the residual factors converged to the values listed in Table 1. A literature search readily revealed isotypism with the compounds listed in Table 2. The refined atomic positions and anisotropic displacement parameters (ADPs) are given in Tables 3 and 4.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe,

Table 3. Atom positions and equivalent isotropic displacement parameters (Å^2) for $NaMn_4(VO_4)_3$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyck. site	x	y	z	U_{eq}
Na1	4*a*	0	1/2	1/4	0.0145(3)
Mn1	8*c*	1/2	0	0.02247(2)	0.00844(8)
Mn2	8*d*	0.26083(5)	1/4	1/8	0.00871(7)
V1	8*d*	1/4	0.15257(4)	7/8	0.00536(7)
V2	4*b*	1/2	1/2	0	0.00563(8)
O1	16*e*	0.29752(15)	0.99798(17)	0.94067(5)	0.0103(2)
O2	16*e*	0.04816(15)	0.27322(16)	0.90028(5)	0.0107(3)
O3	16*e*	0.44671(17)	0.29751(15)	0.04476(5)	0.0113(3)

Table 4. Anisotropic displacement parameters (Å^2) for $NaMn_4(VO_4)_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.0152(4)	U_{11}	0.0133(6)	0	0	0
Mn1	0.00894(13)	0.00790(12)	0.00848(13)	0.00074(12)	0	0
Mn2	0.00894(12)	0.00787(12)	0.00932(14)	0	0	−0.00047(10)
V1	0.00406(12)	0.00644(14)	0.00559(11)	0	0.00012(11)	0
V2	0.00495(12)	U_{11}	0.00699(18)	0	0	0
O1	0.0104(4)	0.0113(4)	0.0090(4)	−0.0001(4)	−0.0015(3)	0.0025(4)
O2	0.0074(4)	0.0105(5)	0.0143(4)	0.0024(3)	−0.0008(3)	−0.0022(4)
O3	0.0140(5)	0.0082(4)	0.0118(4)	0.0002(3)	0.0019(3)	0.0015(3)

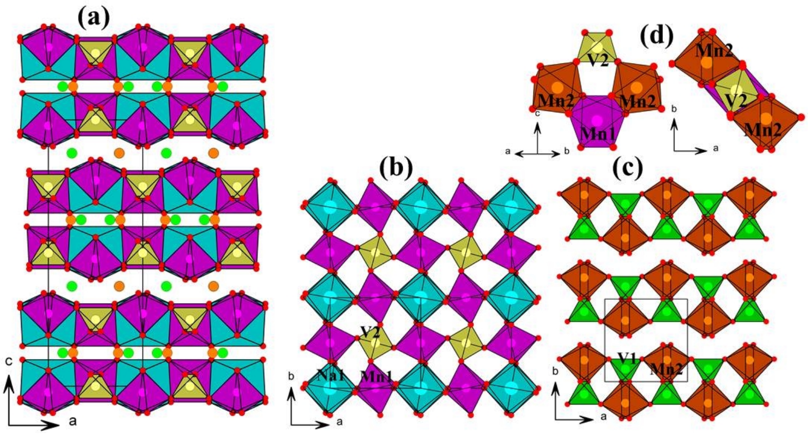

Fig. 3 (color online). (a) Projection views of the crystal structure of $NaMn_4(VO_4)_3$ on the (010) plane; (b) projection view of the sheets present at $z \sim 0$, 1/4, 1/2, and 3/4 on the (001) plane; (c) projection view of the sheets present at $z \sim 1/8$, 3/8, 5/8, and 7/8 on the (001) plane; (d) view of the connections between the ribbons made by Mn1 and V2.

76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-422588.

Structure Description

The crystal structure of $NaMn_4(VO_4)_3$ is isotypic with that of the compounds listed in Table 2. This structure is built up of different sheets stacked perpendicular to the *c* axis (Fig. 3a) [18]. Identical but displaced sheets of polyhedra sit approximately at $z = 0$, 1/4, 1/2, and 3/4. The sheets are square nets with the repeat distance *a*, and with NaO_8 dodecahedra at the corners of the square net. These corners are joined in both directions by the octahedra around Mn1 which share edges with two NaO_8 dodecahedra each. At the center of the square of the net sits a tetrahedron around V2 sharing one vertex with each of the four Mn1 octahedra surrounding it (Fig. 3b).

The sheets are separated by straight double ribbons of polyhedra at $z = 1/8$, 3/8, 5/8, and 7/8. The $V1O_4$ tetrahedron and the $Mn2O_6$ octahedron share a common edge forming thus the basic unit of the ribbons. Each polyhedron shares an edge with the polyhedron of opposite type in the next unit leading to $Mn2V1O_5$ double ribbons. Adjacent ribbons share neither edges nor corners (Fig. 3c). $Mn2O_6$ octahedra in successive ribbons along *a* or *b* are connected with each other by sharing edges with the $Mn1O_6$ octahedra and corners with the $V2O_4$ tetrahedra (Fig. 3d). Interatomic distances and bond valence sums are in good agreement with the expected values (Table 5) [23, 24].

Table 5. Interatomic distances (Å) and bond valence sums BVS [23, 24] for $NaMn_4(VO_4)_3$. The coordination numbers are given in brackets.

	Distance	B.V.[a]
Na1–O1 (4×)	2.3983(10)	0.200
Na1–O2 (4×)	2.7767(11)	0.072
	⟨2.588⟩	BVS [4] = 0.800 BVS [8] = 1.088
Mn1–O1 (2×)	2.1576(10)	0.370
Mn1–O2 (2×)	2.2361(11)	0.299
Mn1–O3 (2×)	2.1685(11)	0.360
	⟨2.187⟩	BVS [6] = 2.058
Mn2–O1 (2×)	2.2612(12)	0.280
Mn2–O2 (2×)	2.1551(11)	0.373
Mn2–O3 (2×)	2.0854(11)	0.450
	⟨2.167⟩	BVS [6] = 2.206
V1–O1 (2×)	1.7284(11)	1.223
V1–O2 (2×)	1.7261(11)	1.231
	⟨1.727⟩	BVS [4] = 4.908
V2–O3 (4×)	1.7180(11)	1.258
		BVS [4] = 5.032

[a] B.V. = $e^{(r0-r)/b}$ with the following parameters: $b = 0.37$, $r_0(Na^I–O) = 1.803$, $r_0(Mn^{II}–O) = 1.790$ and $r_0(V^V–O) = 1.803$.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft. H.B. Y. is indebted to the Alexander von Humboldt Foundation for a research fellowship.

[1] E. Gaudin, H. Ben Yahia, M. Shikano, M. Ben Amara, H.-C. zur Loye, J. Darriet, *Z. Kristallogr.* **2004**, *219*, 755.

[2] J. K. Nimmo, *Acta Crystallogr.* **1981**, *B37*, 431.

[3] S. C. Abrahams, P. Marsh, J. Ravez, *Acta Crystallogr.* **1983**, *C39*, 680.

[4] L. Eddahby, A. Berrada, A. Boukhari, E. M. Holt, *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 527.

[5] H. Müller-Buschbaum, B. Mertens, *Z. Naturforsch.* **1997**, *52b*, 663.

[6] E. Gaudin, H. Ben Yahia, F. J. Zúñiga, J. M. Pérez-Mato, J. Darriet, *Chem. Mater.* **2005**, *17*, 2436.

[7] Y. Le Page, G. Donnay, *Can. Mineral.* **1977**, *15*, 518.

[8] T. I. Krasnenko, L. V. Andrianova, B. V. Slobodin, A. A. Fotiev, V. G. Dobosh, O. A. Zabara, T. P. Sirina, G. D. Milova, A. A. Ivakin, *Russ. J. Inorg. Chem.* **1987**, *32*, 1769.

[9] H. Ben Yahia, E. Gaudin, J. Darriet, *Acta Crystallogr.* **2005**, *C61*, i79.

[10] B. Dickens, W. E. Brown, *Tschermaks Mineral. Petrogr. Mitt.* **1971**, *16*, 1.

[11] H. Yamane, T. Nagasawa, M. Shimada, T. Endo, *Acta Crystallogr.* **1997**, *C53*, 1367.

[12] M. Ben Amara, R. Olazcuaga, G. Le Flem, M. Vlasse, *Acta Crystallogr.* **1979**, *B35*, 1567.

[13] A. P. Tyutyunnik, V. G. Zubkov, L. L. Surat, B. Slobodin, *Russ. J. Inorg. Chem.* **2004**, *49*, 553; *Zh. Neorg. Khim.* **2004**, *49*, 610.

[14] E. V. Murashova, Yu. A. Velikodnyi, V. K. Trunov, *J. Struct. Chem.* **1988**, *29*, 648; *Zh. Strukt. Khim.* **1988**, *29*, 182.

[15] V. Petříček, M. Dušek, L. Palatinus, JANA2006, The Crystallographic Computing System, Institute of Physics, University of Prague, Prague (Czech Republic) **2006**.

[16] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.

[17] H. Abdallah Anissa, A. Brahim, H. Amor, *Acta Crystallogr.* **2004**, *E60*, i77.

[18] R. Gopal, J. S. Rutherford, B. E. Robertson, *J. Solid State Chem.* **1980**, *32*, 29.

[19] N. Krishnamachari, C. Calvo, *Acta Crystallogr.* **1973**, *B29*, 2611.

[20] A. Modaressi, R. Gerardin, B. Malaman, C. Gleitzer, *J. Solid State Chem.* **1984**, *53*, 22.

[21] L. W. Finger, P. G. Conrad, *Am. Mineral.* **2000**, *85*, 1804.

[22] J. Barbier, *Acta Crystallogr.* **1999**, *C55*, IUC9900080.

[23] I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244.

[24] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751.

Druck: AZ Druck und Datentechnik GmbH, Kempten