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Synthesis and Structure of the Ternary Vanadate $\text{NaMn}_4(\text{VO}_4)_3$

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

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The vanadate $\text{NaMn}_4(\text{VO}_4)_3$ was obtained as dark-brown crystals as a side-product during the crystallization of the oxygen-deficient perovskite $\text{Na}_3\text{MnV}_2\text{O}_{7.5}$ in an NaCl/KCl flux. $\text{NaMn}_4(\text{VO}_4)_3$ crystallizes with the tetragonal $(\text{Mg}_{1/2}\square_{1/2})\text{Mg}_4(\text{AsO}_4)_3$ type, space group $I4_2d$. 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 $\text{NaMn}_4(\text{VO}_4)_3$ 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-V₂O₅-Na₂O Ternary System

Introduction

Many different structures have been observed for orthovanadates with the general composition $AB_4(\text{VO}_4)_3$ ($A = \text{Li, Na, K, and Rb}$, and $B = \text{Ca, Mg, and Cd}$). In the $\text{ACd}_4(\text{VO}_4)_3$ series, three different structure types are observed. The structure of $\text{LiCd}_4(\text{VO}_4)_3$ [1] is a modulated variant of the Na_2CrO_4 type [2], $\text{NaCd}_4(\text{VO}_4)_3$ crystallizes with the maricite structure [3], and compounds $\text{ACd}_4(\text{VO}_4)_3$ ($A = \text{K}$ [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 $\text{LiCd}_4(\text{VO}_4)_3$, or $(\text{Li}_{1/3}\text{Cd}_{1/3}\square_{1/3})\text{CdVO}_4$, the Li/Cd disorder induces strong steric strains in the tetrahedral sites and a strong modulation of their occupancies [1, 6].

In $\text{NaCd}_4(\text{VO}_4)_3$, or $(\text{Na}_{1/3}\text{Cd}_{1/3}\square_{1/3})\text{CdVO}_4$, an Na/Ca/vacancy disorder is observed in strongly distorted tetrahedral sites derived from an octahedral site [7]. In $\text{KCd}_4(\text{VO}_4)_3$ [4] and $\text{RbCd}_4(\text{VO}_4)_3$ [5], all sites are fully occupied, but slight Cd/alkali mixing is observed for some of these sites. For the $\text{ACa}_4(\text{VO}_4)_3$ series, only $\text{NaCa}_4(\text{VO}_4)_3$ 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, $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ [10]. The $\text{NaCa}_4(\text{VO}_4)_3$ structure is very similar to that of $\text{Ca}_3\text{Y}_2(\text{SiO}_4)_3$ [11] and $\text{NaCd}_4(\text{PO}_4)_3$ [12], with a silicocarnotite type. In the $\text{AMg}_4(\text{VO}_4)_3$ series, only $\text{LiMg}_4(\text{VO}_4)_3$ [13] and $\text{NaMg}_4(\text{VO}_4)_3$ [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 $\text{AMn}_4(\text{VO}_4)_3$ series, to our knowledge, no compound has been reported in the literature. Herein we report on the successful synthesis and structure of $\text{NaMn}_4(\text{VO}_4)_3$ which is isotopic with $\text{AMg}_4(\text{VO}_4)_3$ ($A = \text{Li, Na}$) [13, 14].

Experimental Section

Synthesis

The title compound was first obtained as a by-product during the crystal growth attempts of $\text{Na}_3\text{MnV}_2\text{O}_{7.5}$ in a NaCl (Merck, > 99.5 %)/KCl (Chempur, > 99.9 %) (1:1 molar ratio) salt flux. $\text{NaMn}_4(\text{VO}_4)_3$ 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 $\text{Na}_3\text{MnV}_2\text{O}_{7.5}$ were also observed.

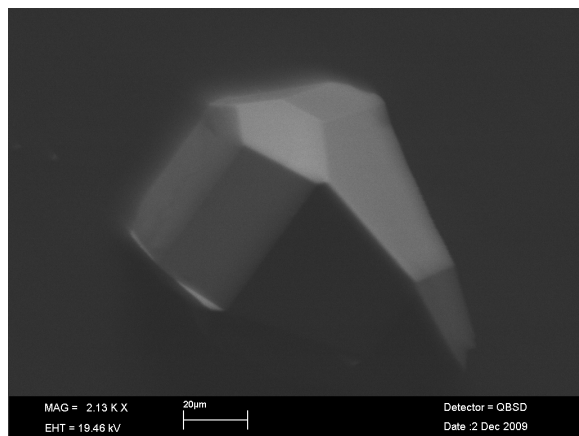


Fig. 1. SEM image of the $\text{NaMn}_4(\text{VO}_4)_3$ single crystal used for the XR data collection.

X-Ray diffraction

At each reaction stage, the polycrystalline sample was characterized by a Guinier pattern (image plate system, Fujifilm BAS-1800) with $\text{CuK}\alpha_1$ 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 $V = 977.70(6)$ Å³.

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 $\text{MoK}\alpha$ 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 diffrac-

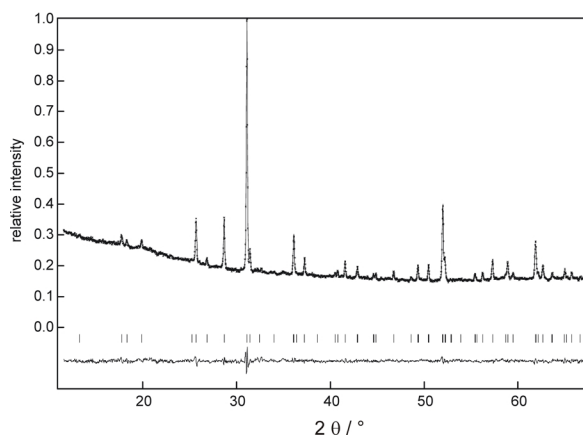


Fig. 2. Observed, calculated and difference plots for the XRPD profile refinement of the $\text{NaMn}_4(\text{VO}_4)_3$ sample.

Table 1. Crystal data and structure refinement for $\text{NaMn}_4(\text{VO}_4)_3$, space group $I\bar{4}2d$, $Z = 4$.

Refined composition	$\text{NaMn}_4(\text{VO}_4)_3$
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	$60 \times 80 \times 110$
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	$\pm 10, \pm 10, \pm 29$
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. Compounds showing the same crystal structure (space group $I\bar{4}2d$, $Z = 4$).

Compounds	a (Å)	c (Å)	V (Å ³)	Ref.
$\text{NaMn}_4(\text{VO}_4)_3$	7.024	19.836	978.6	this work
$\text{NaMg}_4(\text{VO}_4)_3$	6.890	19.292	915.8	[14]
$\text{NaMg}_4(\text{AsO}_4)_3$	6.817	19.242	894.2	[17]
$\text{LiMg}_4(\text{VO}_4)_3$	6.867	18.954	893.8	[13]
$\text{Co}_{1/2}\square_{1/2}\text{Co}_4(\text{AsO}_4)_3$	6.858	18.872	887.6	[18]
$\text{Mg}_{1/2}\square_{1/2}\text{Mg}_4(\text{AsO}_4)_3$	6.783	18.963	872.5	[19]
$\text{Fe}_5(\text{Fe}_{0.17}\text{Ge}_{0.83})_2\text{GeO}_{12}$	6.854	18.747	880.7	[20]
$\text{Mg}_{2.65}\text{Fe}_{0.49}\text{Al}_{1.95}\text{Si}_{2.91}\text{O}_{12}$	6.527	18.183	774.6	[21]
$\text{Ni}_{4.35}\text{As}_3\text{O}_{11.7}(\text{OH})_{0.3}$	6.781	18.835	866.1	[22]

tometer. Details about the data collection are summarized in Table 1.

Structure refinement

The extinction conditions observed for $\text{NaMn}_4(\text{VO}_4)_3$ 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 remaining 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,

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

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)

Table 3. Atom positions and equivalent isotropic displacement parameters (\AA^2) for $\text{NaMn}_4(\text{VO}_4)_3$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Anisotropic displacement parameters (\AA^2) for $\text{NaMn}_4(\text{VO}_4)_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$.

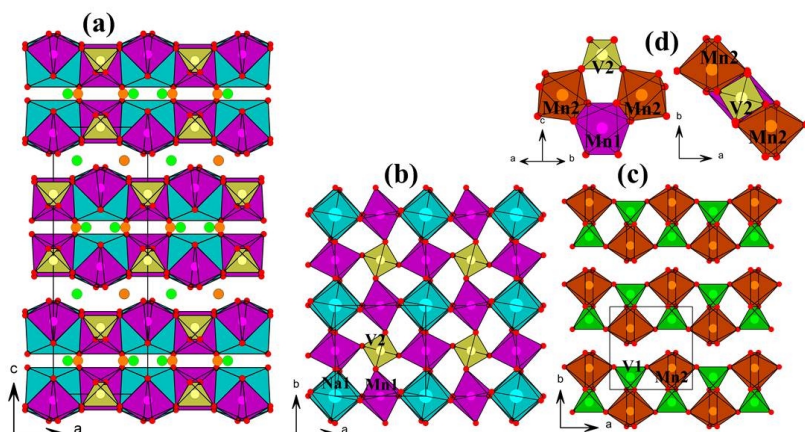


Fig. 3 (color online). (a) Projection views of the crystal structure of $\text{NaMn}_4(\text{VO}_4)_3$ on the (010) plane; (b) projection view of the sheets present at $z \sim 0, 1/4, 1/2,$ and $3/4$ on the (001) plane; (c) projection view of the sheets present at $z \sim 1/8, 3/8, 5/8,$ and $7/8$ on 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 $\text{NaMn}_4(\text{VO}_4)_3$ 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 Mn_2O_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 $\text{Mn}_2\text{V1O}_5$ double ribbons. Adjacent ribbons share neither edges nor corners (Fig. 3c). Mn_2O_6 octahedra in successive ribbons along a or b are connected with each other by sharing edges with the Mn_1O_6 octahedra and corners with the V_2O_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 NaMn₄(VO₄)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) (2.588)	0.072 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) (2.187)	0.360 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) (2.167)	0.450 BVS [6] = 2.206
V1–O1 (2×)	1.7284(11)	1.223
V1–O2 (2×)	1.7261(11) (1.727)	1.231 BVS [4] = 4.908
V2–O3 (4×)	1.7180(11)	1.258 BVS [4] = 5.032

^a B.V. = $e^{(r^0-r)/b}$ with the following parameters: $b = 0.37$, $r_0(\text{Na}^{\text{I}}-\text{O}) = 1.803$, $r_0(\text{Mn}^{\text{II}}-\text{O}) = 1.790$ and $r_0(\text{V}^{\text{V}}-\text{O}) = 1.803$.

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