Journal of Solid State Chemistry **147,** 676–678 (1999)
Article ID jssc.1999.8473, available online at http://www.idealibrary.com on

LETTER TO THE EDITOR

Vanadium(IV)–Oxide Nanotubes: Crystal Structure of the Low-Dimensional Quantum Magnet $Na_2V_3O_7$

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Communicated by H.-C. zur Loye May 18, 1999; accepted August 10, 1999

Fibers of $Na_2V_3O_7$ have been obtained by solid state reaction. This compound crystallizes in the trigonal system, space group *P*31*c*, with $a = 10.886(1)$ Å, $b = 9.5380(1)$ Å, $V = 978.87(2)$, $Z = 6$, and $\rho = 3.163\ \mathrm{g\ cm^{-1}}$. The structure is built up by VO_5 square pyramids connected via edges and apices to form fascinating vanadium(IV)–oxide nanotubes. The cohesion of the network is ensured by the sodium atoms which are located around the nanotubes. The inner diameter of the nanotube is close to 5 Å, which can accommodate the presence of a sodium atom Na1 inside the nanotube. Such geometry with all the vanadium atoms in the valence state IV should give interesting ionic conductivity and magnetic properties.

The interest in low-dimensional quantum magnets arises mainly from a theory of high-temperature superconductivity phenomena still to be discovered. Cuprates are, of course, extensively studied, but the vanadate family recently attracted attention owing to the versatility of the structures and quantum spin phenomena exhibited (1–5). The prototype system is $Na_xV_2O_5$ with $1 \leq x \leq 2$, which includes the spin–Peierls compound NaV_2O_5 (6) and the peculiar zigzag chain $\eta Na_{1.286}V_2O_5$ phase (7). Here we describe the results of our investigation of the rich sodium part of this system, $x > 1.5$, and in particular the crystal structure of $Na_2V_3O_7$, the upper limit ($x = 0$) of a new vanadium bronze $Na_{2-x}V_3O_7$, in which VO_5 square pyramids share edges and corners to form nanotubes. Carbon was first discovered to present such topology (8, 9). Microporous and mesoporous silicates and transition-metal-oxide molecular sieves obtained via the supramolecular templating mechanism can also be viewed as hexagonal close packed arrangement of nanotubes (10–12). However our results provide the first example of transition-metal-oxide nanotubes obtained by solid state reaction.

Single crystals of $Na_2V_3O_7$ were grown under vacuum in a tubular furnace from melts with starting composition $Na_{1.9}V_2O_5$. They grew as very elongated black fibers of a few millimeters in size. One fiber was mounted on an Enraf-Nonius KAPPA CCD single-crystal diffractometer using Mo$K\alpha$ radiation. The cell parameters were determined from the collection of ten images using the program COLLECT (13). Data were collected in the Ω–2θ scan mode up to $2\theta = 54°$. SIR92 (14) was used to solve the structure by direct methods, and the structure was refined using the SHELXL-97 program (15). Because of the poor crystal morphology and quality, only an average structure was obtained and no absorption correction was applied. Crystallographic data are listed in Table 1, and atomic positions and equivalent isotropic temperature factors are given in Table 2.

A projection of the structure along 0*z* is presented in Fig. 1. All the vanadium atoms are in the oxidation state IV and are surrounded by five oxygen atoms to form square pyramids with characteristically short vanadyl bonds V1–O1, V2–O2, and V3–O3 of lengths 1.637(15), 1.637(7), and 1.628(18) Å, respectively. Unexpectedly, these pyramids are connected via edges and apices to form these fascinating nanotubes. The sodium atoms Na2, Na3, and Na4 located around the tubes ensure the cohesion of the network, while Na1 is situated in the middle of the tube. The idealized representation of the unfolded nanotube in Fig. 2a allows a simplistic description of the vanadium polyhedra arrangement. If one takes into account only the short vanadium–vanadium distances V1–V2 = 2.905(5) Å and V1–V3 = 2.979(2) Å, the 3 atoms V1–V2–V3 form a basic structural unit. Three of these units connected by edges, i.e., nine square pyramids, are needed to form a slice (A). It is worth mentioning that the goemetry of this slice is reminiscent of that of vanadium oxides with the same formulation MV_3O_7 obtained by hydrothermal reaction in the presence of

0022-4596/99 $30.00

TABLE 1

Crystallographic Data for $Na_2V_3O_7$

Formula	$Na_2V_3O_7$
System	Trigonal
Space group	$P31c$ (no. 159)
Crystal size (mm)	$0.013 \times 0.015 \times 0.3$
a (Å)	10.886 (1)
c (Å)	9.5380 (1)
V (Å^3)	978.87 (2)
Z	6
Calculated density (g cm^{-3})	3.163
μ (cm^{-1})	43.3
Reflections collected	16969
Independent reflections	1989
Observed reflections $I > 2\sigma(I)$	1666
Refined parameters	52
$R = \sum \lVert F_o\rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$	0.0874
$R_w = [\sum_w (\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2 / \sum_w (F_o^2)^2]^{1/2}$	0.1533

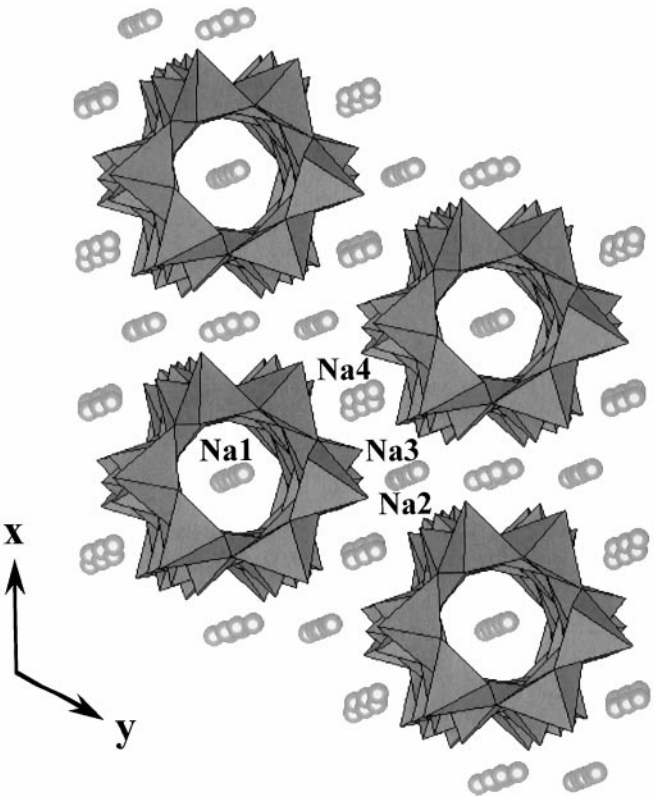

FIG. 1. The crystal structure of $Na_2V_3O_7$ projected along [001]. The VO_5 square pyramids are represented in dark gray. The filled circles are Na atoms. Na2 and Na3 are located at the same positions x and y but at different heights z.

organic cations (e.g., $M =$ methylammonium cation $CH_3NH_3^+$ or tetramethylammonium $N(CH_3)_4^-$) (16, 17), except that in $Na_2V_3O_7$ all the apices of the square pyramids are pointing in the same direction (out from the nanotube), while they alternate two up then two down in the latter compounds. The tube can be obtained by bringing the points M and N in contact. The next slice (B) obtained via the c-glide plane along c is connected by corner sharing to the (A) slices. The vanadium-oxide nanotube is thus formed by the repetition (A) (B) (A) (B)… along 0z (Fig. 2b). The inner diameter of the nanotube is close to 5 Å, which means that on the removal of sodium atoms Na1 this compound can be classified as a microporous material like synthetic zeolites. The Na1 atoms which lie along the center of the nanotube are bonded to six oxygen atoms located at 2.372(14) and 2.585(13) Å which form a flattened trigonal antiprism. The sequence along the c axis is successively one antiprism occupied by Na1, one more complicated empty polyhedron which could probably accommodate larger ions such as K^+, Rb^+, Cs^+, and so on. Na2 and Na3 located on a threefold axis are bonded to the apices O1, O2, and O3 of the vanadium square pyramids. In this way they strengthen the network since they link three nanotubes. Their coordination polyhedron $Na2[O1O2]_3$ and $Na3[O2O3]_3$ are distorted trigonal antiprisms which are associated in pairs by sharing the edge $[O2]_3$ and which are separated along the [001] direction by an empty octahedron $[O1O3]_3$. The sodium Na4 located close to (1/2, 1/2, 1/3) is surrounded by six oxygen atoms at a distance ranging from 2.36 to 2.97 Å, which form a very distorted polyhedron, the description of which is beyond the scope of this letter.

TABLE 2

Fractional Atomic Coordinates and Thermal Parameters for $Na_2V_3O_7$

Atom	x	y	z	U_{eq} (Å^2)
V1	0.3146(3)	0.1154(3)	0	0.0035(5)
V2	0.3154(2)	0.1518(4)	0.3496(5)	0.0069(4)
V3	0.3147(5)	0.1918(4)	0.7000(3)	0.0136(8)
Na1	0	0	0.124(2)	0.066(4)
Na2	1/3	2/3	0.039(2)	0.030(5)
Na3	1/3	2/3	0.6722(14)	0.002(3)
Na4	0.4908(11)	0.5107(11)	0.3364(10)	0.0347(14)
O1	0.4757(15)	0.1534(15)	0.0420(18)	0.011(3)
O2	0.4891(7)	0.2371(17)	0.351(2)	0.0121(16)
O3	0.4766(17)	0.3148(16)	0.665(2)	0.016(4)
O4	0.3029(13)	0.0380(12)	− 0.1873(14)	0.006(2)
O5	0.2506(12)	0.0712(12)	0.5333(14)	0.002(3)
O6	0.2424(14)	0.1661(14)	0.1671(17)	0.014(3)
O7	0.2514(13)	0.2924(15)	0.3942(16)	0.0119(18)

Note. Origin at (0, 0, 0).

From a magnetic point of view, this structure provides the first example of a spin $\frac{1}{2}$ ladder-like system with periodic boundary conditions in the rung direction. Such systems are expected to behave very differently from standard ladders with open boundary conditions in the rung direction if the number of legs is odd: Standard ladders are gapless (18), while periodic ladders should exhibit a gap (19, 20). The

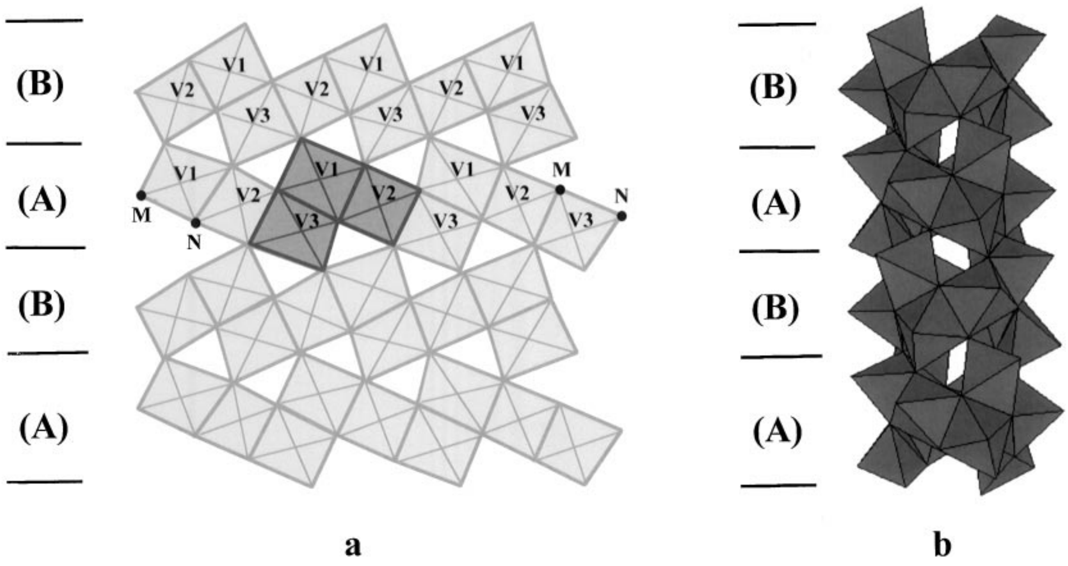

FIG. 2. Idealized representation of the unfolded vanadium-oxide nanotube (a). The basic structural unit V1–V2–V3 is in dark gray. Three units make the ring (A), and the nanotube represented in (b) is made by putting M and N into contact and by repeating the sequence (A) (B) (A) … along the *c* axis.

present nanotube has nine sites per ring, but it is likely that the effective model will indeed be a three-legged ladder since these sites are arranged in units involving three vanadium atoms. Work is in progress, both theoretically and experimentally, to study the magnetic properties of this system.

Aside from the magnetic properties, interesting ionic conductivity properties can be expected for compounds with different amounts of sodium ions located around or within the nanotubes. Exchange reactions are currently in progress on this fascinating compound.

ACKNOWLEDGMENT

The authors thank the CNRS for financial support.

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