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Synthesis and structural characterization of sodium vanadyl(IV) orthophosphate $NaVOPO_4$

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Abstract. A new sodium vanadyl(IV) orthophosphate $NaVOPO_4$ has been synthesized by solid-state and hydrothermal method and characterized by single-crystal X-ray diffraction and magnetic susceptibility. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.524(1)$, $b = 8.455(4)$, $c = 7.119(1)$, $\beta = 115.29(1)^\circ$, $Z = 4$, $R = 0.027$, and is structurally similar to the triclinic analog $LiVOPO_4$. The structure can be described as close-packed infinite chains of trans-corner-sharing VO_6 octahedra with the holes around each chain filled with Na and P atoms. These infinite chains have alternating short and long V–O bonds and are similar to those found in β-$VOPO_4$. The Na atom has six close oxygen neighbors at distances of 2.268 to 2.511 Å.

Introduction

Lavrov et al. (1982) reported the crystal structure of $LiVOPO_4$ which consists of chains of distorted VO_6 octahedra sharing opposite corners, and orthophosphate groups connecting them. Recently Phillips et al. (1990) reported the crystal structure and optical properties of $KVOPO_4$, which is isostructural with the well-known nonlinear optical material $KTiOPO_4$. Since the nature of alkali metal cations plays an important role in the crystal structures of these phosphates, it would be interesting to synthesize and structurally characterize the Na analog. As part of our program in the synthesis and characterization of new solid-state phosphates, we have determined that $NaVOPO_4$ is structurally similar to $LiVOPO_4$. Herein, we report the synthesis, crystal structure, and magnetic susceptibility of this new compound.

Experimental

Crystals of $NaVOPO_4$ were obtained from solid-state or hydrothermal method. In solid-state method, a stoichiometric mixture of Na_3PO_4 (AESAR), VO_2 (Cerac), and P_2O_5 (Cerac) was pelletized in a nitrogen-filled glove box, and then sealed in an evacuated silica tube. Olive-green crystals of $NaVOPO_4$ for crystal structure analysis were grown by heating the reaction mixture at 850° C for 12 h, slowly cooled to 750° C, maintained at 750° C for 24 h, and then furnace-cooled to room temperature. A single-phased polycrystalline sample for magnetic measurements was obtained by heating the stoichiometric mixture at 750° C for 2 d with an intermediate grinding. The X-ray powder pattern of the olive-green polycrystalline product compared well with that calculated from the single-crystal data. In the hydrothermal method, a mixture of 1.53 g $Na_4V_2O_7$ (Cerac) and 0.75 g V_2O_3 (Cerac) (molar ratio $Na:V = 1:1$) was added to 10 ml of 7.5 M H_3PO_4 and sealed in a 23-ml Teflon-lined autoclave (Parr Instruments). The reaction vessel was maintained at 230° C and autogenous pressure for 3 d before slow cooling to room temperature. It was found that, in addition to the olive-green crystals of $NaVOPO_4$, unknown black crystalline materials also crystallizes from the reaction.

An olive-green crystal having the dimensions 0.10 × 0.10 × 0.25 mm was selected for indexing and intensity data collection at 24° C on a Nicolet R3m/V diffractometer with graphite-monochromated MoKα radiation. The intensities of three reflections were monitored and no significant decay was detected. The reflections were corrected for Lorentz and polarization effects, but no absorption corrections were applied. The structure was solved by direct methods and successive Fourier syntheses in the space group $P2_1/c$, and refined by full-matrix least-squares refinement based on F values. All of the atoms were refined with anisotropic temperature factors. All calculations were performed on a DEC MicroVAX II computer system using SHELXTL-Plus programs (Sheldrick, 1990). Data collection and refinement parameters are collected in Table 1. Final positional and thermal parameters are listed in Table 2. Selected interatomic distances are given in Table 3.[1]

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[1] Additional material to this paper can be ordered referring to the no. CSD 54607, name(s) of the author(s) and the title of the paper at the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 1. Summary of crystal data, intensity measurements, and refinement parameters for $NaVOPO_4$.

1. Crystal data	
Space group	$P2_1/c$
Cell constants	$a = 6.524(1)$, $b = 8.455(4)$, $c = 7.119(1)$ Å, $\beta = 115.29(1)°$, $V = 355.0(2)$ Å^3
Z	4
Density (calcd)	3.459 g/cm^3
2. Intensity measurements	
λ (Mo $K\alpha$)	0.71073 Å
Scan mode	$\theta/2\theta$
Scan rate	2.93–14.95°/min
Scan width	1.1° + $K\alpha_1$, α_2 separation
Maximum 2θ	50°
Standard reflns	3 every 50 reflns (no decay)
Reflections with $I > 2.5\ \sigma(I)$	568
3. Structure solution and refinement	
Parameters refined	74
Agreement factors	$R = 0.027$, $R_w = 0.030$
GOF	1.195
$(\Delta\varrho)_{max}$; $(\Delta\varrho)_{min}$	0.36 e/Å^3, −0.44 e/Å^3

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (Å^2 × 100) for $NaVOPO_4$.

Atom	x	y	z	U_{eq}
Na	0.2473(2)	−0.0876(2)	0.2164(2)	2.59(6)
V	0.74645(8)	0.73811(6)	0.02878(8)	1.06(3)
P	0.2496(1)	0.93431(9)	−0.2516(1)	0.98(3)
O(1)	0.2508(3)	0.1790(2)	0.2526(3)	1.31(8)
O(2)	0.5712(3)	0.1796(2)	0.1007(3)	1.47(8)
O(3)	0.3556(3)	0.4625(2)	0.1336(3)	1.32(8)
O(4)	−0.0614(3)	0.3279(2)	−0.0921(3)	1.39(7)
O(5)	0.1535(3)	0.0398(2)	−0.1293(3)	1.33(8)

Note. Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Variable-temperature magnetic susceptibility $\chi(T)$ data were obtained from 4 to 300 K in a magnetic field of 3 kG using a Quantum Design SQUID magnetometer on 315.51 mg of polycrystalline sample. Diamagnetic contributions for Na^+, V^{4+}, P^{5+}, and O^{2-} were estimated according to Selwood (1956), which were subtracted from the experimental suscepti-

Table 3. Selected bond distances (Å) for $NaVOPO_4$.

V−O(1)a	2.130(3)	V−O(1)b	1.627(2)
V−O(2)a	1.999(2)	V−O(3)a	2.000(2)
V−O(4)a	1.986(2)	V−O(5)a	2.016(2)
P−O(2)a	1.541(2)	P−O(3)c	1.546(3)
P−O(4)d	1.545(2)	P−O(5)e	1.553(3)
Na−O(1)	2.268(3)	Na−O(5)	2.511(3)
Na−O(2)f	2.378(3)	Na−O(3)f	2.381(3)
Na−O(4)g	2.338(3)	Na−O(5)g	2.449(3)

Symmetry codes: a: $1-x, 1-y, -z$; b: $1-x, 1/2+y, 1/2-z$; c: $x, 3/2-y, -1/2+z$; d: $-x, 1/2+y, -1/2-z$; e: $x, 1+y, z$; f: $1-x, -1/2+y, 1/2-z$; g: $-x, -y, -z$.

bility data to obtain the molar susceptibilities of the compound. The data were least-squares fitted from 50 to 300 K to the relation $x_M = C/(T-\theta)$, where C is the molar Curie constant and θ is the Weiss constant.

Description of the structure and discussion

Two drawings of the structure along the *a*- and *c*-axis are shown in Figures 1 and 2, respectively. The title compound and $LiVOPO_4$, which are structurally similar, crystallize in space groups $P2_1/c$ and $P\bar{1}$, respectively. The unit cell volume is approximately 3.5% larger than that of the Li analog, reflecting the larger radius of the Na atom. The framework of the title compound is built of infinite chains of trans-corner-sharing VO_6 octahedra along the *c*-axis, which are linked together by PO_4 groups. These infinite chains have alternating short and long V−O bonds. Each phosphate group bonds to two adjacent octahedra in one chain, and two octahedra in two neighboring chains, introducing "kinks" into the $\cdot\cdot V=O\cdot\cdot V=O\cdot\cdot$ chains. The bond angle at the shared O atoms, O(1), between two V atoms is 142.9(1)°, which is greater than the corresponding angles (139, 136°) in the Li analog. It would be interesting to compare the way in which the vertices are shared in the title compound with those in α-$VOPO_4$ (Jordan and Calvo, 1973) and β-$VOPO_4$ (Gopal and Calvo, 1972). In both polymorphs of $VOPO_4$ each tetrahedron shares all its vertices with octahedra and each octahedron shares four vertices with tetrahedra and two with other octahedra. In α-$VOPO_4$ each phosphate group links four ReO_3-type chains forming a 3D structure. In β-$VOPO_4$ each phosphate group shares its vertices with four VO_6 octahedra but two of these belong to the same chain, so that "kinks" are also introduced into the $\cdot\cdot V=O\cdot\cdot V=O\cdot\cdot$ chains. The chains in the title compound are similar to those found in β-$VOPO_4$. In both $NaVOPO_4$ and β-$VOPO_4$ each phosphate group links three chains as compared with four in α-$VOPO_4$. The structure

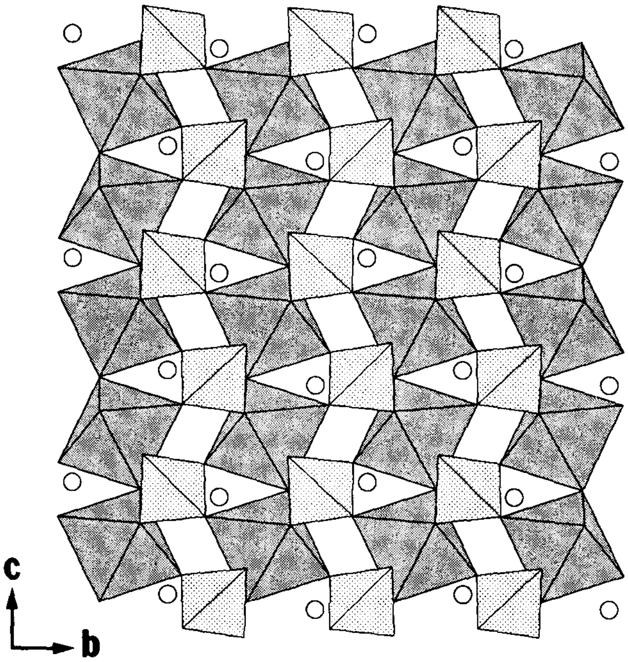

Fig. 1. A polyhedral representation of the $NaVOPO_4$ structure along the *a*-axis.

of $NaVOPO_4$ can also be regarded as close-packed chains along the *c*-axis with the holes around each chain filled with Na and P atoms.

The VO_6 groups in $NaVOPO_4$ are distorted. The V atom is displaced 0.238 Å out of the least-squares plane through the four equatorial oxygen atoms towards the apical oxygen atom O(1). The V – O(1) distances are 1.627(2) and 2.130(3) Å while the equatorial V – O bond lengths are 1.986(2) – 2.016(2) Å long. The very short V – O bond is characteristic of the vanadyl ion VO^{2+}, which has a strong bond with both σ and π character.

The coordination number (CN) of Na^+ can be determined by the maximum Na – O distance, L_{max}, that will still be considered a bond according to the procedure of Donnay and Allmann (1970) with the revised radii of Shannon (1976), leading to 3.19 Å. Accordingly, Na^+ may be considered as being coordinated by seven oxygen atoms with the Na – O distances ranging from 2.268(3) to 2.941(3) Å. The Na – O bond distances can be divided into four groups: a very short distance at 2.268(3) Å, three medium distances ranging from 2.338(3) to 2.381(3) Å, two longer distances at 2.449(3) and 2.511(3) Å, and a very long one at 2.941(3) Å. The very short Na – O bond involves the bridging oxygen atom, O(1), and is considerably shorter than the value 2.40 Å for a six-coordinate Na calculated from

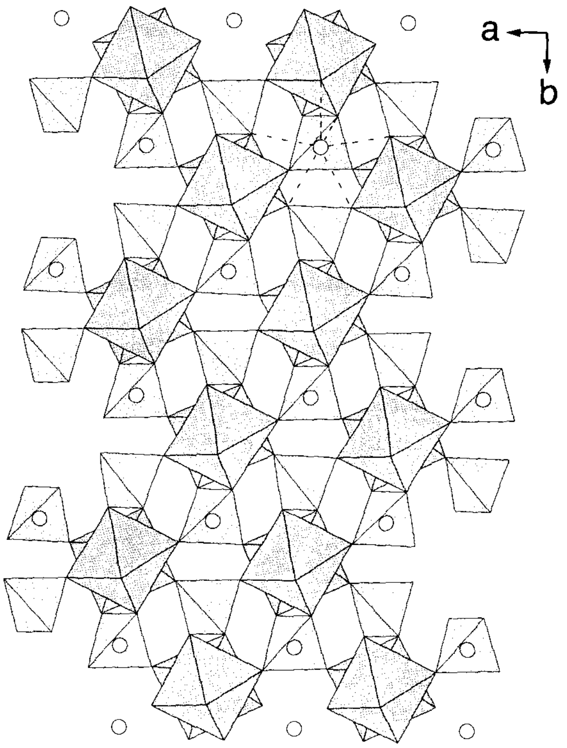

Fig. 2. A polyhedral representation of the $NaVOPO_4$ structure along the *c*-axis. The Na—O bonds are represented by dashed lines.

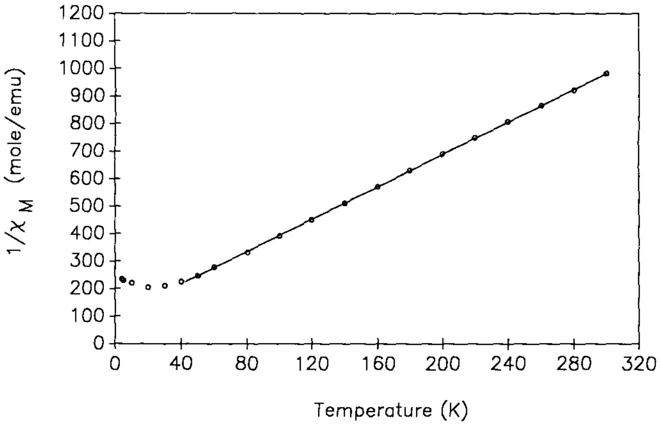

Fig. 3. Inverse molar magnetic susceptibility of $NaVOPO_4$ vs. temperature.

crystal radii. The very large gap between the sixth and seventh bonds suggests that one can consider the coordination of Na as six instead of seven. Bond valence sum of the six Na – O bonds using the formula derived by Brown and Altermatt (1985) is equal to 1.26, which is higher than the expected value 1.0. The Na site in the title compound appears too small to accommodate K cation so that $KVOPO_4$ adopts a different structural type.

A plot of the reciprocal molar susceptibility for polycrystalline $NaVOPO_4$ vs. temperature (Fig. 3) is linear above ~50 K. The solid line in the figure is the fit of the data from 50 to 300 K according to $x = C/(T-\theta)$ with the Curie constant $C = 0.340\ \mathrm{cm}^3 \cdot \mathrm{K/mol}$ and the Weiss constant $\theta = -34$ K. From the relation $C = N\mu_{\mathrm{eff}}^2/3k_B$ one obtains the effective magnetic moment $\mu_{\mathrm{eff}} = 1.65\ \mu_B$, which is close to the value of $1.73\ \mu_B$ calculated for V^{4+} ions with $S = 1/2$ and $g = 2$. The magnetic interactions responsible for the deviation of the data below ~50 K from the Curie-Weiss fit are antiferromagnetic.

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