

Synthesis and characterization of an open framework vanadium silicate (VSH-16Na)

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Abstract

A new sodium vanadium(III) silicate, $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$ (VSH-16Na¹) has been synthesized hydrothermally and its structure determined by single crystal X-ray diffraction. The compound crystallizes in the triclinic space group $\text{P}\bar{1}$ with $a = 7.524(1)$ Å, $b = 8.755(2)$ Å, $c = 9.055(2)$ Å, $\alpha = 62.486(3)^\circ$, $\beta = 83.998(3)^\circ$, $\gamma = 88.692(3)^\circ$, $V = 525.9(2)$ Å³, and $Z = 2$. The $[\text{SiO}_4]$ tetrahedra share corners with each other to form unbranched $[\text{Si}_8\text{O}_{22}]^{12-}$ double chains. These chains are connected by isolated $[\text{VO}_6]$ octahedra to form an open framework structure with eight-ring channels. The magnetic susceptibility data show Curie–Weiss behavior down to 5 K and are consistent with the trivalent state of the vanadium atoms.

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1. Introduction

Recently, new classes of open-framework materials constructed from tetrahedral and other polyhedral building units have gained considerable interest [1]. Such frameworks can provide many properties similar to those of traditional zeolites such as microporosity, size and shape selectivity, and thermal stability. In addition, the presence of transition metal ions in framework sites may provide catalytically active sites [2].

We are interested in vanadium silicates because frameworks with higher stability than the corresponding phosphates can be obtained. By using hydrothermal techniques, we have succeeded in synthesizing several novel alkali metal vanadium silicate phases, some of which are microporous [3]. We recently reported the synthesis and structures of two of these new open framework vanadosilicates VSH-1 and VSH-2 (Vanadium Silicates Houston- n) [4].

As part of our systematic investigation, we report the synthesis and structure of a new vanadium(III) silicate $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$ (VSH-16Na¹) that has vanadium atoms in octahedral coordination and “unbranched vierer double

chains” of composition $[\text{Si}_8\text{O}_{22}]_n^{12n-}$ [5]. To our knowledge, no vanadium(III) silicate phases synthesized under mild hydrothermal conditions have been previously reported although the dense phase NaVSi_2O_6 [6] with a structure similar to that of jadeite ($\text{NaAlSi}_2\text{O}_6$) is well known.

2. Experimental

2.1. Materials and methods

All the chemicals used for the reactions were commercial reagent grade and were used as purchased. Elemental analysis was performed at Galbraith Laboratories, Knoxville, TN. The infrared spectrum was recorded on a Galaxy FT-IR 5000 Series spectrometer from 4000 to 400 cm^{-1} using the KBr pellet method. Thermogravimetric analysis was carried out using a TA Instruments Hi-Res 2950 thermogravimetric analyzer. A powder sample of VSH-16Na was analyzed over a temperature range of 25–500 °C with a heating rate of 5 °C/min in flowing dry N_2 . Magnetic data were measured in the range 5 K < T < 300 K, $H = 0.5$ T, on a Quantum Design MPMS SQUID XL Magnetometer. The diamagnetic correction was estimated from Pascal’s constants to be -159×10^{-6} $\text{emu}\cdot\text{mol}^{-1}$ per formula unit [7,8].

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¹ The notation VSH- nA is used to identify a series of new vanadium silicate frameworks, VSH stands for Vanadium Silicate Houston, n is the series number and A is the non-framework cation.

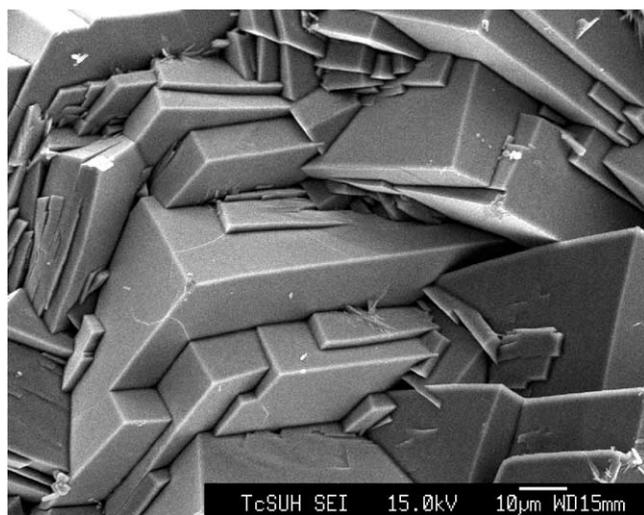


Fig. 1. Scanning Electron Micrograph of Crystals of $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$, VSH-16Na.

2.2. Synthesis

The synthesis of VSH-16Na was carried out in a 23 ml Teflon-lined autoclave under hydrothermal conditions. Sodium orthovanadate (0.3678 g, 2 mmol, Alfa), 45% aqueous NaOH (0.35 ml, 1.5 mmol, Aldrich), sodium silicate solution (1.5 ml, 9.36 mmol, contains 14% NaOH, ~ 27% SiO_2 , Aldrich), and deionized H_2O (3 ml) were mixed together and stirred thoroughly. The resulting clear solution was sealed together with a small piece of vanadium metal (V^0) and heated at 230 °C under autogenous pressure for 8 days. Green crystals of VSH-16Na were obtained by vacuum-filtration as an almost pure phase (yield > 99%). A scanning electron micrograph of typical VSH-16Na crystals is shown in Fig. 1.

2.3. Crystal structure analysis

The crystal structure was determined by single crystal X-ray diffraction. Data were collected using a Siemens SMART platform diffractometer fitted with 1K CCD area detector and graphite monochromatized Mo- $K\alpha$ radiation at ambient temperature. The data were integrated using the Siemens SAINT program [9], with the intensities corrected for Lorentz factor, polarization, air absorption and absorption due to variation in the path length through the detector faceplate. The program SADABS was used for the absorption correction [10].

The structure was solved with direct methods and refined by using the SHELXTL program [11]. All non-hydrogen atom positions were refined anisotropically in the final refinements. The hydrogen atoms were located from the difference maps and refined isotropically. The crystallographic data are listed in Table 1. Atom positions are given in Table 2 and selected bond lengths and bond angles in Table 3.

Table 1
Crystallographic data of VSH-16Na

Formula	$\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$
Formula weight	426.29
Crystal system	Triclinic
Space group	P-1 (no. 2)
Unit cell dimensions	$a = 7.5238(14) \text{ \AA}$ $\alpha = 62.486(3)^\circ$ $b = 8.755(2) \text{ \AA}$ $\beta = 83.998(3)^\circ$ $c = 9.055(2) \text{ \AA}$ $\gamma = 88.692(3)^\circ$
Volume, Z	$525.9(2) \text{ \AA}^3, 2$
Temperature	293(2) K
Wavelength	0.71073 \AA
Absorption coefficient	1.589 mm^{-1}
Reflections collected	3063
Independent reflections	2269 [R(int) = 0.0474]
Goodness of fit	0.896
Final R indices [I > 2σ(I)]	$R_1 = 0.0433, wR_2 = 0.0845$
R indices (all data)	$R_1 = 0.0937, wR_2 = 0.0966$
(Δρ) _{max} : (Δρ) _{min} (e/Å ³)	0.598, -0.544

$$R_1 = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}, wR_2 = \frac{[\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2}}{w = 1/[\sigma^2(F_0^2) + (0.809)^2 + 24.17P]}; \text{ where } P = [\max(F_0^2, 0) + 2F_c^2]/3.$$

3. Results and discussion

3.1. Structure description

The compound is triclinic with space group $\bar{P}1$. The crystal structure is built up from VO_6 octahedra and SiO_4 tetrahedra (Fig. 2). There are Si–O–Si and Si–O–V bonds, but no V–O–V bonds. Each of the V^{III} atoms (V1 and V2) is bonded to six oxygen atoms that are further bonded to silicon atoms. The isolated $[\text{VO}_6]$ octahedra are slightly distorted; the V–O bond lengths vary from 1.950 Å to 2.144 Å with an average of 2.04 Å. No unusually short V–O distances that would indicate the presence of V^{IV} or V^{V} cationic species are present. Charge balance and a bond valence sum calculation indicate the presence of only V(III), and this is confirmed by magnetic measurements.

The silicate tetrahedra form a double chain of composition $\text{Si}_4\text{O}_{11}^{6-}$ with a chain periodicity of four (Fig. 3). The double chain contains equal numbers of Q^3 ($\text{SiO}_3/2\text{O}_{1/1}$) and Q^2 ($\text{SiO}_2/2\text{O}_{2/1}$) tetrahedra and can be called an “unbranched vierer double chain” according to Liebau’s classification [5].

In VSH-16Na, the unbranched silicate double chains run along the [100] direction (Fig. 3). $[\text{VO}_6]$ octahedra join the silicate chains to form the open framework. Eight-ring channels are observed along the [100] direction with a free aperture of $6.0 \times 2.6 \text{ \AA}$. Seven-ring channels are also found parallel to [1 1 0] direction (Figs. 4, 5). The framework possesses a formal charge of -3 per unit formula. This charge is balanced by the presence of hydrated sodium ions inside the channels.

‘Unbranched vierer double chains’ similar to that of VSH-16Na were recently reported in the niobium silicate

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for VSH-16Na

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq.)*
V(1)	0	5000	0	9(1)
V(2)	5000	0	0	9(1)
Si(1)	2230(2)	2896(2)	3188(2)	9(1)
Si(2)	1148(2)	925(2)	1542(2)	9(1)
Si(3)	3946(2)	7461(2)	-1685(2)	9(1)
Si(4)	2626(2)	909(2)	-3049(2)	9(1)
Na(1)	1438(3)	7355(3)	1391(3)	22(1)
Na(2)	3408(3)	-1459(3)	4276(3)	23(1)
Na(3)	3681(3)	3956(3)	-1734(3)	18(1)
O(1)	2248(5)	2489(5)	5144(5)	14(1)
O(2)	963(5)	2806(5)	7(4)	10(1)
O(3)	3976(4)	1593(4)	-2222(5)	11(1)
O(4)	4319(5)	-2135(4)	-191(5)	12(1)
O(5)	963(5)	4456(4)	2283(5)	11(1)
O(6)	4319(5)	3324(5)	2363(5)	16(1)
O(7)	2675(4)	-284(4)	1355(5)	10(1)
O(8)	-708(5)	-217(5)	1950(5)	14(1)
O(9)	1534(5)	1122(4)	3218(5)	12(1)
O(10)	3562(5)	9329(4)	-3349(5)	12(1)
O(11)	2306(5)	6157(5)	-1245(5)	13(1)
OW	2083(6)	-4270(6)	5550(6)	30(2)
H(1)	1048(52)	-4533(70)	6318(61)	26(18)
H(2)	1713(88)	-3924(85)	4476(45)	49(25)

* *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3

Selected bond lengths (Å) for VSH-16Na

V(1)–O(11) × 2	1.980(4)	Si(4)–O(1) ⁱⁱ	1.633(4)
V(1)–O(2) × 2	2.033(3)	Si(4)–O(10) ⁱ	1.657(4)
V(1)–O(5) × 2	2.100(4)		
V(2)–O(7) × 2	1.977(4)	Na1–O7 ^v	2.271(6)
V(2)–O(4) × 2	2.030(4)	Na1–O5	2.305(6)
V(2)–O(3) × 2	2.065(4)	Na1–O2 ^{vi}	2.354(6)
		Na1–O4 ^v	2.418(6)
		Na1–O8 ^v	2.838(7)
Si(1)–O(5)	1.587(4)	Na1–O8 ^{vi}	2.999(8)
Si(1)–O(1)	1.639(4)	Na2–OW	2.379(7)
Si(1)–O(6)	1.641(4)	Na2–O7	2.475(6)
Si(1)–O(9)	1.637(4)	Na2–O9	2.480(7)
Si(2)–O(7)	1.595(4)	Na2–O10 ^{vii}	2.556(6)
Si(2)–O(2)	1.605(4)	Na2–O3 ^{viii}	2.605(6)
Si(2)–O(8)	1.645(4)	Na2–O10 ^{iv}	2.780(7)
Si(2)–O(9)	1.660(4)	Na3–O3	2.308(6)
Si(3)–O(11)	1.591(4)	Na3–O11	2.362(6)
Si(3)–O(4) ^v	1.608(4)	Na3–O2	2.376(7)
Si(3)–O(6) ^{iv}	1.652(4)	Na3–O4 ^{viii}	2.375(7)
Si(3)–O(10)	1.679(4)	Na3–O6 ^{iv}	2.642(7)
Si(4)–O(3)	1.599(4)	Na3–OW ^{ix}	2.647(8)
Si(4)–O(8) ⁱⁱⁱ	1.618(4)		

Symmetry codes:

ⁱ *x*, -1 + *y*, *z*; ⁱⁱ *x*, *y*, -1 + *z*; ⁱⁱⁱ -*x*, -*y*, -*z*; ^{iv} 1 - *x*, 1 - *y*, -*z*; ^v *x*, 1 + *y*, *z*; ^{vi} -*x*, 1 - *y*, -*z*; ^{vii} *x*, -1 + *y*, 1 + *z*; ^{viii} 1 - *x*, -*y*, -*z*; ^{ix} *x*, 1 + *y*, -1 + *z*.

Na₂H(NbO)Si₄O₁₁·1.25H₂O [12]. A noticeable difference between the silicate chains of the two structures is their degree of stretching. The silicate chain in the niobium compound is highly stretched with a length of 9.1 Å per period while in VSH-16Na the corresponding length is

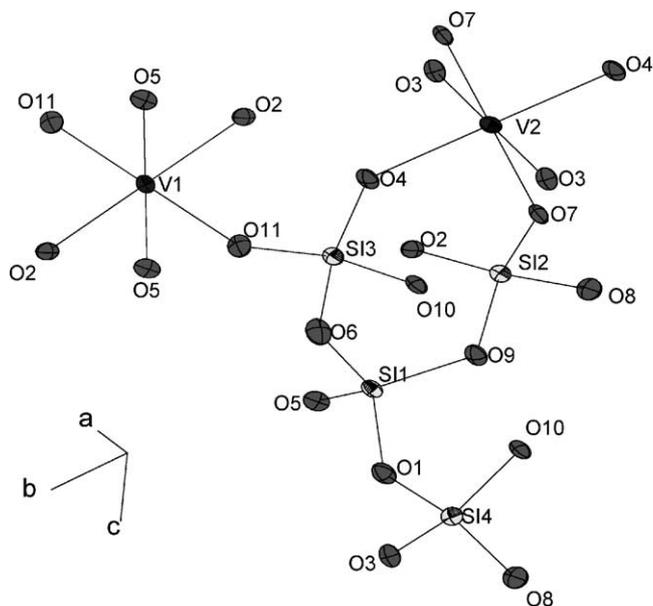


Fig. 2. Coordination environments of V and Si in VSH-16Na. Thermal ellipsoids are drawn with 50% probability.

7.5 Å. As a consequence, the chain in the latter is better described as being a tube formed by folding interconnected six-rings while the former more closely resembles a ribbon. In the niobium compound, each NbO₆ octahedron shares five corners with silicate tetrahedra from three double chains. Only one or two tetrahedra from each chain are connected to the same NbO₆ octahedron. In contrast, in the structure of VSH-16Na the VO₆ octahedron links two silicate double

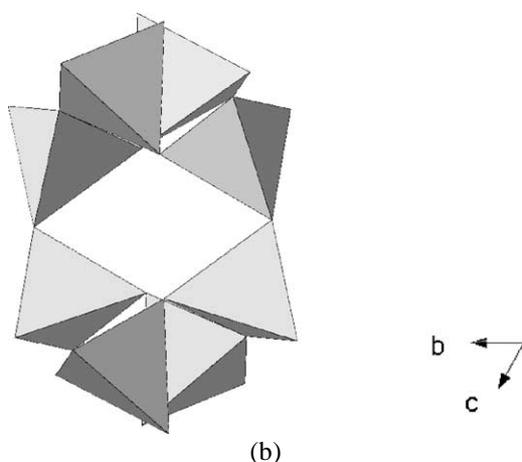
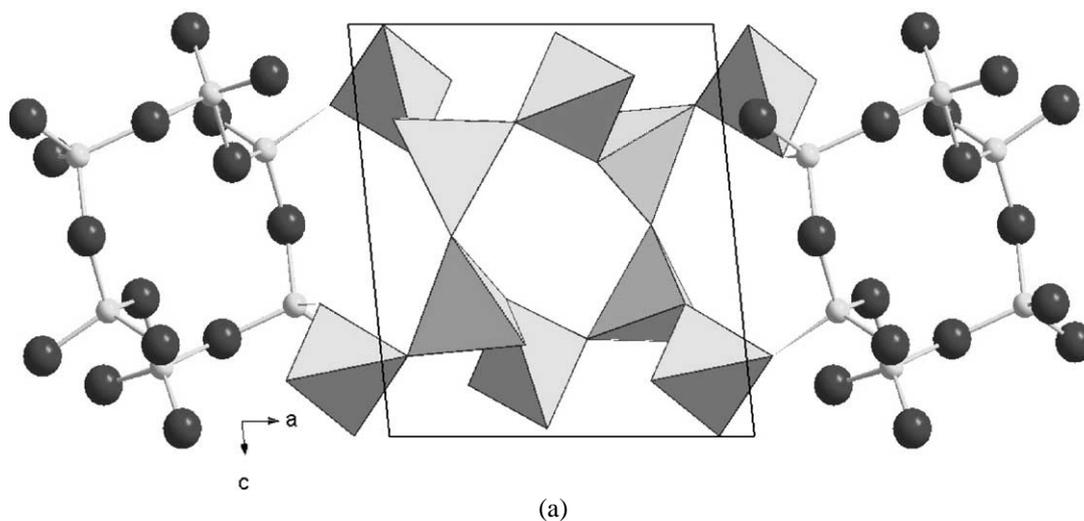


Fig. 3. The double silicate chain found in $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$.

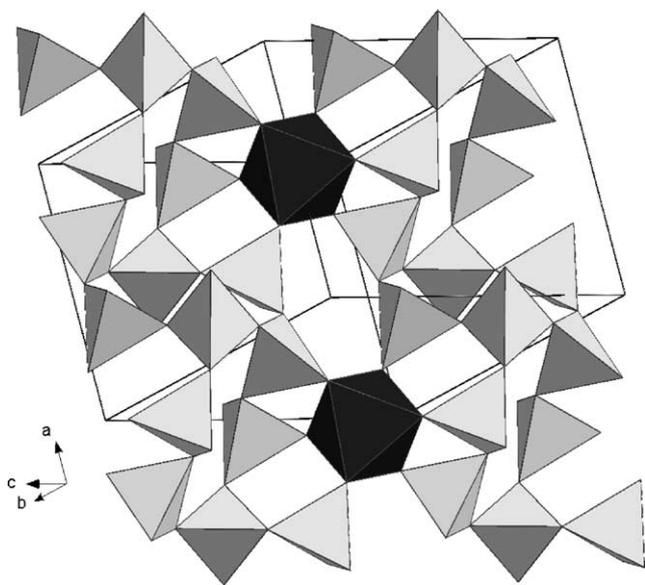


Fig. 4. Two double chains connected by VO_6 octahedra in $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$.

chains by sharing corners with three tetrahedra from each chain. Therefore, the tetrahedra are pulled closer to each other by the VO_6 octahedra, which results in the lower degree of stretching found in the chains in VSH-16Na.

There are three symmetry independent Na sites. Na2 and Na3 cations exhibit similar distorted octahedral coordination environments. Both of them are coordinated by five O atoms and one H_2O group at distances ranging 2.379–2.780 Å for Na2–O and 2.308–2.647 Å for Na3–O, respectively. The Na1 site is coordinated by seven O atoms, with four short Na–O distances (2.271–2.419 Å) in a distorted tetrahedral configuration and long Na–O distances (2.838 Å and 3.031 Å, respectively) which indicate weaker bonding. The water molecules are located within the eight-ring channels. Relatively strong hydrogen bonds occur between the water oxygen and O5 atoms (O12w...O5: 2.81 Å, H1...O5: 1.89 Å). The O6 atom, which has the highest U_{eq} value among the framework oxygen atoms (Table 2), is bonded to two silicon (Si1, Si3) atoms and one sodium (Na3) atom in a planar triangle configuration. The displacement ellipsoid of O6 is considerably elongated along the direction perpendicular to the triangle plane. Refinements of models with splitting of the O6 position were unsuccessful. The bond valence sum calculated for O6 (1.98 v.u.) agrees well with the formal oxidation state.

3.2. Characterization

Thermogravimetric analysis (Fig. 6) shows a weight loss in the range 100–420 °C corresponding to the removal of 1.03 H_2O per formula unit. The result is in good agreement with the stoichiometry $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$ determined from the X-ray structure analysis. The powder X-ray diffraction patterns measured before and after the TGA experiment show close similarity, indicating that the framework is stable up to ~ 500 °C. However, no substantial re-hydration was observed when the sample was heated up to ~ 500 °C in dry nitrogen flow and subsequently cooled off in a mixture

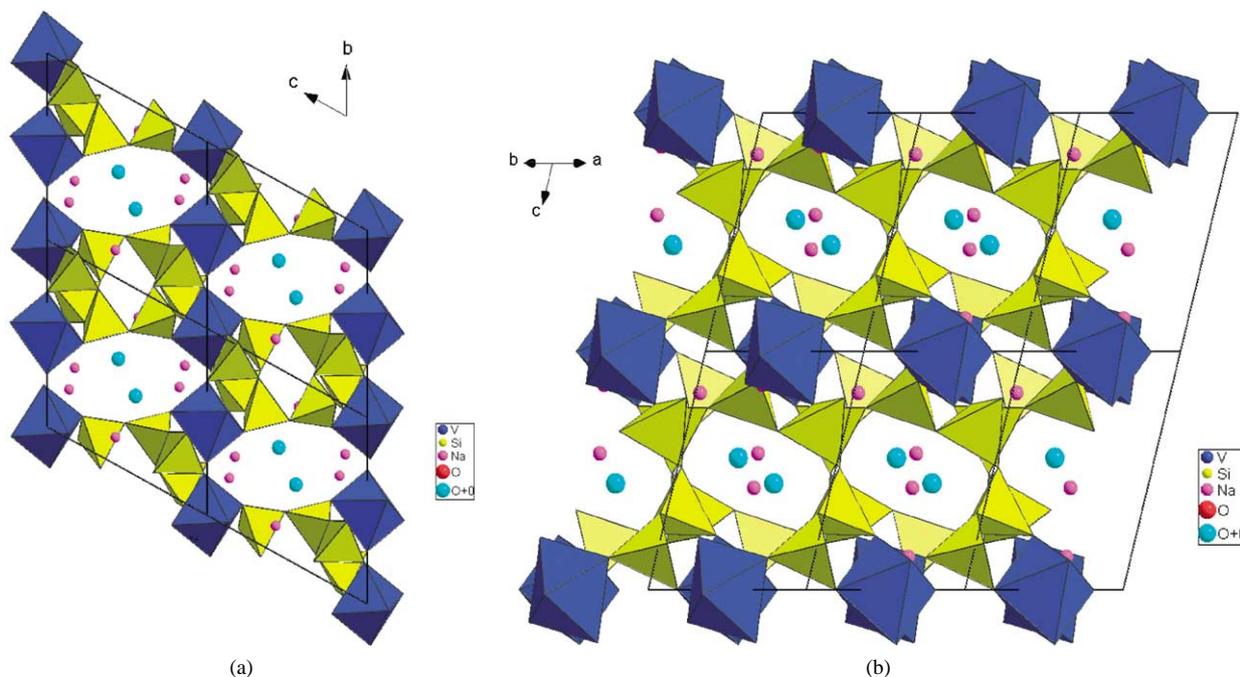


Fig. 5. Two views of the structure of $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$ (a) along [100], (b) along [110] showing the eight and seven member rings.

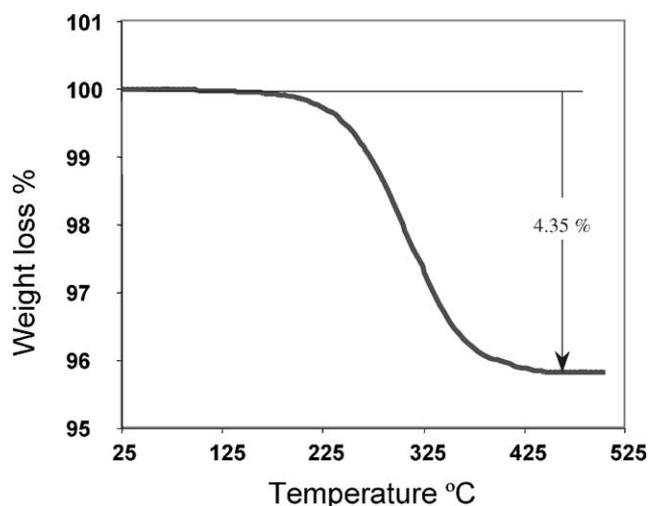


Fig. 6. Thermogravimetric analysis data for $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$.

of water vapor and nitrogen in the TGA experiments. The irreversibility of dehydration could be due to adjustment of the structure, in particular, the Na positions upon removal of the water molecules. The elemental analyses gave 16.26% Na, 26.48% Si, 11.97% V in good agreement with the calculated percentages of 16.18% Na, 26.36% Si, 11.95% V for $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$.

The IR spectrum of VSH-16Na shows vibration modes for Si–O and V–O at 1103, 1016, 954, 896, 773, 757, 561, 462, 426 cm^{-1} . Additional absorption bands for O–H bending and stretching vibrations are observed at 3529, 3062, 1672 cm^{-1} .

3.3. Magnetic data

The temperature-dependence of the magnetic susceptibility of VSH-16Na has been measured in the range of 5–300 K. Data were fit over the complete temperature range according to the Curie–Weiss law, $\chi_m = \chi_0 + C/(T - \theta)$. In this equation, θ is the Weiss constant and χ_0 is the temperature independent susceptibility (estimated to be $-159 \times 10^{-6} \text{ emu}\cdot\text{mol}^{-1}$ from Pascal's constants). A good fit is obtained with $C = 0.804 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ and $\theta = -2.34 \text{ K}$. The effective magnetic moment is 2.55 BM, which is in the range expected for isolated V(III) ions. No long-range magnetic interactions are observed as expected since the nearest V–V distance is 5.706 Å. This observation is consistent with the oxidation state of vanadium derived from charge balance and bond valence sum calculations (2.82 v.u. for V) [13].

4. Conclusions

A new vanadium(III) silicate was synthesized in single-crystal form by a hydrothermal method. The compound $\text{Na}_3\text{V}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$ (VSH-16Na) contains “unbranched vierer double chains” with the composition $[\text{Si}_8\text{O}_{22}]^{12-}$. The double chains are linked by VO_6 octahedra to form an open framework structure. The magnetic susceptibility data shows Curie–Weiss behavior consistent with the presence of isolated V(III) O_6 octahedra. VSH-16Na is the first member of the VSH- n series that contains V^{3+} . Several vanadium(III) phosphates, such as $\text{CsVHP}_3\text{O}_{10}$ [14], $\text{CsV}_2\text{P}_5\text{O}_{16}$ [15], and $\text{Cs}_3\text{V}_3\text{P}_{12}\text{O}_{36}$ [16] have been reported that have related structures. They contain isolated octahedral V(III) O_6 units

in which all of the oxygen atoms are shared with phosphate tetrahedra. Unlike in the VSH-16Na structure where the linking tetrahedra form chains, in the phosphate structures the tetrahedra polymerize into discrete units (trimers and pentamers) in CsVHP₃O₁₀ and CsV₂P₅O₁₆, and a twelve membered ring in Cs₃V₃P₁₂O₃₆.

Acknowledgements

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References

- [1] J. Rocha, M.W. Anderson, *Eur. J. Inorg. Chem.* 2000 (2000) 801.
- [2] G. Perego, R. Millini, G. Bellussi, in: H.G. Karge, J. Weitkamp (Eds.), *Molecular Sieves: Science and Technology*, Vol. 1, Springer-Verlag, Berlin, New York, 1998, p. 181.
- [3] X. Wang, L. Liu, A.J. Jacobson, *J. Amer. Chem. Soc.* 124 (2002) 7812 (published as advanced article on the web, 6th June 2002).
- [4] X. Wang, L. Liu, A.J. Jacobson, *Angew. Chem. Int. Ed. Engl.* 40 (2001) 2174.
- [5] F. Liebau, *Structural Chemistry of Silicates*, Springer-Verlag, Berlin, Heidelberg, 1985.
- [6] H. Ohashi, T. Osawa, A. Sato, *Acta Crystallogr., Sect. C* 50 (1994) 1652.
- [7] O. Kahn, *Molecular Magnetism*, VCH, New York, USA, 1993.
- [8] L.N. Mulay, E.A. Boudreaux, *Theory and Applications of Molecular Diamagnetism*, Wiley-InterScience, 1976.
- [9] Siemens Analytical X-ray Instruments, SAINT, Version 4.05, Madison, WI, 1995.
- [10] G.M. Sheldrick, SADABS, Program for Siemens Area Detector Absorption Corrections, University of Göttingen, Germany, 1997.
- [11] G.M. Sheldrick, SHELXTL, Program for Refinement of Crystal Structure, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.
- [12] M.A. Salvadó, P. Pertierra, S. García-Granda, S.A. Khainakov, J.R. García, A.I. Bortun, A. Clearfield, *Inorg. Chem.* 40 (2001) 4368.
- [13] E. Brese, M. O’Keeffe, *Acta Crystallogr., Sect. B* 47 (1991) 192.
- [14] B. Klinkert, M. Jansen, *Z. Anorg. Allg. Chem.* 567 (1988) 77.
- [15] B. Klinkert, M. Jansen, *Z. Anorg. Allg. Chem.* 567 (1988) 87.
- [16] A.V. Lavrov, V.P. Nikolaev, G.G. Sadikov, M.J. Vojtenkov, *Dokl. Akad. Nauk SSSR* 259 (1981) 103.