

Structural transformations in the $\text{Na}_{4+x}\text{VO}(\text{PO}_4)_2$ vanadylphosphates

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Abstract

The crystal structures of new sodium vanadylphosphate, $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ ($a = 15.4450(11)\text{Å}$, $b = 14.7690(10)\text{Å}$, $c = 6.9870(5)\text{Å}$, $Z = 8$, S.G. *Ibam*), and new (γ -) modification of $\text{Na}_4\text{VO}(\text{PO}_4)_2$ ($a = 15.4455(15)\text{Å}$, $b = 14.8433(10)\text{Å}$, $c = 7.0081(5)\text{Å}$, $Z = 8$, S.G. *Pbc2_1*) have been investigated by X-ray single-crystal diffraction. Both structures contain isolated infinite chains of the corner-sharing VO_6 octahedra. The octahedra within the chains are additionally linked to each other by the tetrahedral PO_4 groups. Sodium atoms are situated in the positions between the chains. Depending on the conditions of synthesis, the number of sodium atoms in the unit cell of the $\text{Na}_{4+x}\text{VO}(\text{PO}_4)_2$ compounds may vary resulting in a change of the oxidation state of vanadium atoms and a change of their coordination environment. In $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ vanadium atoms have almost regular octahedral coordination with six close V–O separations and all chains in the structure are equivalent. The crystal structure of $\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$ contains two non-equivalent chain types: the first one is similar to that found in $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ whereas the second one contains VO_6 octahedra with the short vanadyl bonds. The charge redistribution was supposed in the new γ -modification of $\text{Na}_4\text{VO}(\text{PO}_4)_2$ where the $\text{V}^{4+\delta}$ and $\text{V}^{4-\delta}$ cations orderly occupy octahedral positions in different chains. The origin of this phenomena is discussed.

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1. Introduction

Recently, we have reported the synthesis and properties of the new sodium vanadylphosphate $\text{Na}_4\text{VO}(\text{PO}_4)_2$ [1]. This compound undergoes a reversible phase transition around 200 °C. The crystal structure of the low-temperature $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$ modification contains isolated infinite chains of corner-sharing VO_6 octahedra and sodium atoms orderly situated between the chains. The V–O bonds inside the octahedra are not equal to each other: there are four close equatorial distances about 2 Å, one shortened due to a vanadyl bond formation apical distance (about 1.7 Å) and one elongated (opposite to vanadyl distance) with a bond length > 2 Å. The reversible phase transition from β - to α -form is accompanied by the transformation from primitive to body-centered unit cell and the change in ionic

conductivity by the order of magnitude. Detailed electron diffraction investigation revealed that diverse superstructures may exist in $\text{Na}_4\text{VO}(\text{PO}_4)_2$. We suggested that these superstructures could result from the different ordering types appearing due to alternative distributions of the Na atoms between the chains or due to different orientations of the vanadyl bonds inside the VO_6 octahedra in the neighboring chains. The complexity of ordering in a similar crystal structure type has been demonstrated earlier during the investigation of the sodium titanil(IV)phosphate, $\text{Na}_4\text{TiO}(\text{PO}_4)_2$ [2]. This compound also exhibits several polymorph modifications with different distributions of sodium atoms. High temperature modifications are known to behave as superionic conductors with sodium atoms randomly occupying positions between the chains that results in a high mobility of the cations [3]. At low temperatures the distribution of sodium cations becomes completely ordered thus leading to commensurately and incommensurately modulated structures [4–6].

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Herein we present the results of the investigation of isotypical $\text{Na}_{4+x}\text{VO}(\text{PO}_4)_2$ compounds and analysis of their structural features induced by different factors such as sodium content and vanadyl bond orientation in comparison with the parent $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$ structure.

2. Experimental

Green single-phase powder of $\text{Na}_4\text{VO}(\text{PO}_4)_2$ was synthesized by a solid-state reaction between stoichiometric mixture $\text{Na}_4\text{P}_2\text{O}_7$ and VO_2 (in molar ratio 1:1) in evacuated and sealed quartz ampoules by annealing at 700°C for 3 days followed by furnace cooling. Single crystals for structure analysis were taken from the different samples obtained by melting of as-prepared powder in evacuated and sealed quartz tubes at 730°C followed by slow cooling. No visible traces of interaction with quartz surface were observed. Dark-gray and pale-gray crystals were separated from green material ($\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$) and selected for X-ray data collection. Sodium content was found from the results of crystal structure solution and refinement.

Data collections for the single-crystal structure refinement were performed using a CAD4 diffractometer for $\text{Na}_4\text{VO}(\text{PO}_4)_2$ and a Bruker APEX CCD X-ray diffractometer equipped with CRYO-FLEX low temperature attachment for $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$. Structure computations were made with JANA2000 program package [7]. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 415859 and 415860.

Differential scanning calorimetric (DSC) measurements were performed using Netzsch STA-409 thermoanalyser with heating and cooling rates of $10^\circ\text{C}/\text{min}$ in closed Al_2O_3 crucible in dry helium atmosphere. The kaolin was used as a reference material.

3. Results

3.1. Crystal structure of $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$

The reflections from pale-grey single crystal were indexed in an orthorhombic unit cell with lattice parameters $a = 15.4450(11)$, $b = 14.7690(10)$, $c = 6.9870(5)\text{Å}$, $Z = 8$. Assuming, that the titled compound is isotypical with $\text{Na}_4\text{TiO}(\text{PO}_4)_2$: *Ibam*, $a = 15.647(8)$, $b = 14.989(8)$, $c = 7.081(5)\text{Å}$ [2], the latter crystal structure was used as a starting model for the refinement. Sodium atoms were localized from the series of different Fourier maps. Their occupancies were refined initially with fixed and then together with atomic displacement parameters. This revealed the full occupancy for Na(3) and Na(4) positions only, whereas the other Na positions were found to be partially occupied. The final refinement was carried out with anisotropic displacement parameters (ADP) for all atoms. The sodium content was refined as 4.35(3) per

formula unit giving the overall composition $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$. The average oxidation state of vanadium atom in this structure is +3.65. Crystallographic data are listed in Table 1. The atomic coordinates with isotropic displacement parameters and selected interatomic distances in the $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ structure are listed in Tables 2 and 3, respectively.

This structure is closely related to that of $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$ and it is shown in Fig. 1. Zigzag-like infinite chains of the corner-sharing VO_6 octahedra run along the *c*-direction of the unit cell. Within each chain the octahedra are additionally linked to each other by phosphate groups. Every PO_4 group is connected via two vertexes while other two vertexes are bonded only with sodium atoms. All chains in the structure are equivalent. Sodium atoms are located between the chains and are only partially ordered.

The main differences between the structures of $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ and $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$ (the possible reasons for these differences will be discussed below) are in the positions of vanadium atoms within the octahedra and in the placement of sodium atoms between the chains. The VO_6 octahedron has four almost equal V–O equatorial distances of 1.9988(14) and 2.0113(14) Å to O(6) and O(7) atoms, respectively. Two apical V–O(1) distances are 1.8750(7) Å. The polyhedra around sodium atoms are of two different types (Fig. 2). The first type represents polyhedra of the Na(1) and Na(2) atoms, which are isolated distorted square pyramids. The second group

Table 1
Summary of crystallographic information for $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ and $\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$

Parameter/composition	$\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$	$\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$
Molecular weight	356.9	348.85
Crystal system	Orthorhombic	
Space group	<i>Ibam</i> [72]	<i>Pbc2₁</i> [29]
<i>a</i> (Å)	15.4450(11)	15.444(2)
<i>b</i> (Å)	14.7690(10)	14.846(4)
<i>c</i> (Å)	6.9870(5)	7.0077(14)
Volume (Å ³)	1593.79(19)	1606.7(2)
<i>Z</i>	8	
<i>D</i> _{calc} (g cm ⁻³)	2.974	2.883
Radiation, wavelength (Å)	MoK α , 0.71073	
Temperature (K)	70	293
μ (cm ⁻¹)	1.916	1.881
Color	Pale-grey	Dark-grey
Diffractometer	Bruker	CAD4
Counter	CCD	Scintillation
No. of measured/independent reflection ($I \geq 3\sigma$)	6700/869	9127/3175
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>k</i> → 22 0 → <i>h</i> → 25 -11 → <i>l</i> → 11	-26 → <i>h</i> → 26 0 → <i>k</i> → 25 0 → <i>l</i> → 12
Refinement	on F	
Absorption correction	Multi-scan	<i>psi</i> -scan
<i>R</i> / <i>R</i> _w ($I > 3\sigma(I)$)/GOF	0.030/0.044/1.59	0.029/0.043/1.94
No. of refined parameters	104	317
Weighting scheme, (Δ/σ) _{max}	Sigma	
$\Delta\rho$ _{max} (e ⁻ /Å ⁻³) positive/negative	0.70/-0.66	0.74/-0.56

Table 2
Atomic positions and occupancies for Na_{4.35}VO(PO₄)₂

Atom		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>G</i>
V	8 <i>e</i>	1/4	1/4	3/4	0.01471(19)	1
P(1)	8 <i>j</i>	0.37817(5)	0.11975(5)	1/2	0.0114(2)	1
P(2)	8 <i>j</i>	0.11804(5)	0.12193(4)	1/2	0.0077(2)	1
Na(1)	8 <i>j</i>	0.38056(11)	0.11652(12)	0	0.0220(6)	0.779(5)
Na(2)	8 <i>j</i>	0.11721(10)	0.13658(10)	0	0.0101(5)	0.742(5)
Na(3)	8 <i>g</i>	0.23478(10)	0	3/4	0.0235(4)	1
Na(4)	8 <i>f</i>	1/2	0.23147(10)	3/4	0.0239(4)	1
Na(5)	8 <i>g</i>	0.0258(3)	1/2	3/4	0.0299(15)	0.342(5)
Na(6)	8 <i>f</i>	0	0.02070(15)	3/4	0.0182(9)	0.488(4)
O(1)	8 <i>j</i>	0.25532(11)	0.20419(14)	0	0.0148(6)	1
O(2)	8 <i>j</i>	0.10808(13)	0.01897(12)	1/2	0.0159(6)	1
O(3)	8 <i>j</i>	0.02970(13)	0.16838(13)	1/2	0.0163(6)	1
O(4)	8 <i>j</i>	0.33298(13)	−0.02843(14)	0	0.0167(6)	1
O(5)	8 <i>j</i>	0.52336(13)	0.11178(13)	0	0.0168(6)	1
O(6)	16 <i>k</i>	0.35333(9)	0.17522(10)	−0.31840(19)	0.0177(4)	1
O(7)	16 <i>k</i>	0.16906(9)	0.14820(10)	−0.31741(18)	0.0143(4)	1

Table 3
Selected interatomic distances (Å) for Na_{4.35}VO(PO₄)₂

Atom–Atom	Distance	Atom–atom	Distance
V–O(1) × 2	1.8750(7)	Na(2)–O(1)	2.355(2)
V–O(6) × 2	1.9988(14)	Na(2)–O(2)	2.302(2)
V–O(7) × 2	2.0113(14)	Na(2)–O(3)	2.317(3)
P(1)–O(4)	1.519(2)	Na(2)–O(7) × 2	2.3641(14)
P(1)–O(5)	1.526(2)	Na(3)–O(2) × 2	2.6380(19)
P(1)–O(6) × 2	1.5582(14)	Na(3)–O(4) × 2	2.3511(17)
P(2)–O(2)	1.5283(19)	Na(3)–O(7) × 2	2.4582(15)
P(2)–O(3)	1.527(2)	Na(4)–O(3) × 2	2.3344(16)
P(2)–O(7) × 2	1.5488(13)	Na(4)–O(5) × 2	2.5112(17)
Na(1)–O(1)	2.328(3)	Na(4)–O(6) × 2	2.4597(15)
Na(1)–O(4)	2.263(3)	Na(5)–O(4) × 2	2.826(4)
Na(1)–O(5)	2.207(3)	Na(5)–O(5) × 2	2.4037(13)
Na(1)–O(6) × 2	2.4244(15)	Na(5)–O(5) × 2	2.5203(19)
		Na(6)–O(2) × 2	2.4163(14)
		Na(6)–O(2) × 2	2.4862(15)
		Na(6)–O(3) × 2	2.832(2)

contains all other NaO_{*n*} polyhedra that are connected via common edges or faces. The Na(3) and Na(4) atoms are situated in the distorted octahedra. These octahedra form infinite chains along the *c*-direction by sharing the common O(2)–O(4) or O(5)–O(3) edges for Na(3)O₆ and Na(4)O₆, respectively. Randomly filled positions of the Na(5) and Na(6) atoms are located in a distorted cube. The cubes are connected through one of their quadrilateral faces forming wide quadrangle channels that run along the *c*-direction. These positions should provide for ionic conductivity of Na_{4.35}VO(PO₄)₂. Phosphorus atoms exhibit almost regular tetrahedral coordination with the typical P–O distances of 1.52–1.56 Å.

3.2. Crystal structure of γ -Na₄VO(PO₄)₂

The sample obtained by melting of Na₄VO(PO₄)₂ contained dark-grey (black in reflected light) crystals, one of which was chosen for X-ray single crystal experiment.

The unit cell parameters, $a = 15.4455(15)$, $b = 14.8433(10)$, $c = 7.0081(5)$ Å, $\alpha = \beta = \gamma = 90^\circ$, were refined based on 24 high angle reflections. The analysis of systematic extinctions allowed to suggest the *Pbcm* or *Pbc2*₁ space groups. Atomic coordinates of the β -Na₄VO(PO₄)₂ structure (taking into account the multiplicity of corresponding positions) were used as the starting structural model. Structure refinement in the centrosymmetric *Pbcm* space group did not allow to obtain the *R*-value lower than 10%, therefore, non-centrosymmetric *Pbc2*₁ space group was chosen for further structure solution. Partially occupied positions of sodium atoms were found from the series of difference Fourier maps. For the final refinement the occupancy parameters for some sodium atoms were fixed as 1.0 if they were > 1.0 or differ from 1 less than 2 σ . A weak electron density peak (about 3.5 $\bar{e}/\text{\AA}^3$) was located near the position of the V(2) atom. Since the V(2) atom was found to be shifted from the square plane of the V(2)O₆ octahedron due to the formation of short vanadyl bond, the existence of two orientations for the vanadyl bond was supposed. Occupancies of the V(2) and V(3) positions were refined with their sum constrained to unity. Final occupancies were found to have the values close to 0.8 and 0.2 for V(2) and V(3), respectively. An attempt to remove the less occupied position led to an increase of the *R*-value by 2.5%. The final refinement was carried out in the *Pbc2*₁ space group in anisotropic approximation for all atoms; the corresponding parameters for V(2) and V(3) were constrained. Among 10 positions for the sodium atoms only those of Na(2), Na(5) and Na(6) were fully occupied, whereas the others were only partially filled. As a result, the refined composition is Na_{4.01(4)}VO(PO₄)₂ (here and further we call it γ -form to distinguish from α - and β -modifications reported in [1]), and the vanadium oxidation state remains as +4.0. The EDX analysis revealed the V:P ratio as 1:2, however this technique is not precise enough to determine the sodium content. Crystallographic data for γ -Na₄VO(PO₄)₂ are listed in Table 1. The refined atomic

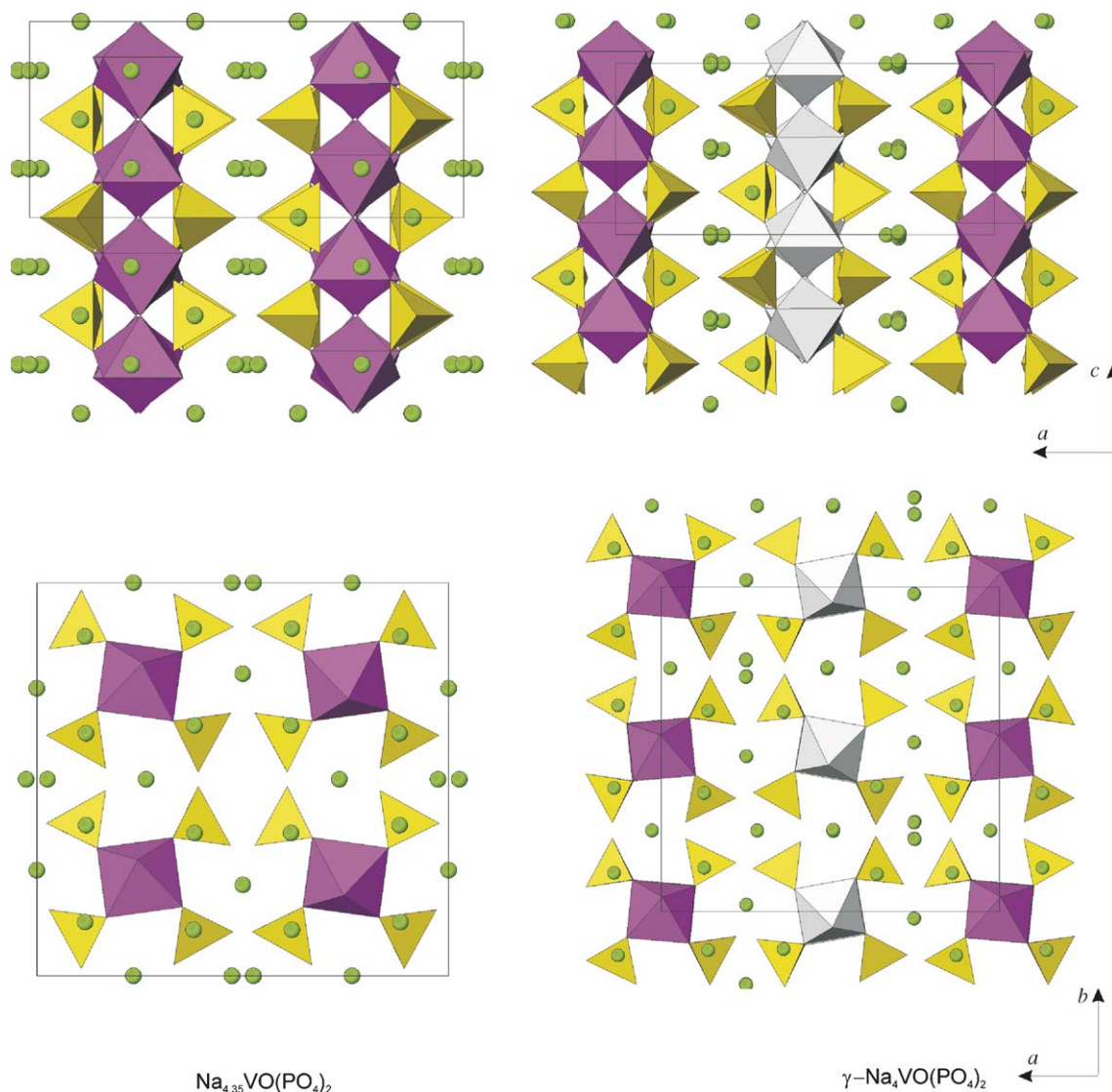


Fig. 1. Two projections of the $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ and $\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$ crystal structures. Circles represent sodium atoms. Two different chains in $\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$ are shown by lighter and darker octahedra.

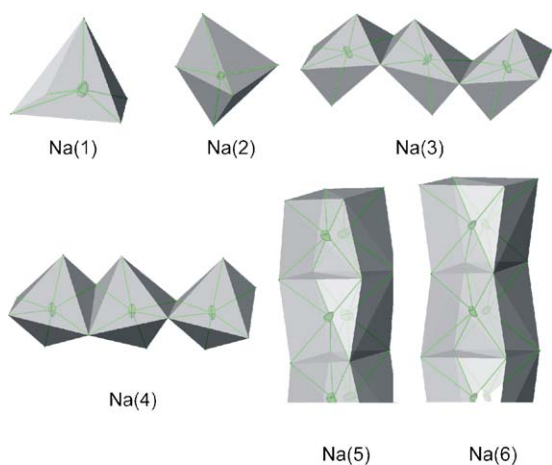


Fig. 2. Coordination polyhedra of the Na atoms and their connections in $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$.

parameters and selected interatomic distances are given in Tables 4 and 5, respectively.

Structural motif of $\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$ is close to that of $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ or $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$. However, there are certain distinctions that make this structure unique among the other $\text{Na}_4\text{MO}(\text{PO}_4)_2$ ($M = \text{Ti}, \text{V}, \text{Fe}$ [8]) compounds. The major difference between the γ - and β -modifications is the presence of two types of chains formed by corner-sharing VO_6 octahedra in the former structure (Fig. 1). The distinction between these chains in the unit cell requires the reduction of symmetry from $Pbca$ (for $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$) down to $Pbc2_1$. One of the chains contains the $\text{V}(1)\text{O}_6$ octahedra which are similar to those found in the $\text{Na}_{4.35}\text{MO}(\text{PO}_4)_2$ structure. Four equatorial $\text{V}(1)\text{-O}$ distances are in the range of 1.994(4)–2.027(4) Å, whereas the apical $\text{V}(1)\text{-O}(1)$ separations are as short as 1.882(3) and 1.871(3) Å (Fig. 3a). Another type of chain is formed by the

Table 4
Atomic positions and occupancies for Na₄VO(PO₄)₂

Atom	x	y	z	U _{eq} (Å ²)	Occupancy
V(1)	0.00045(12)	0.50000(5)	0.5	0.01172(12)	1
V(2)	0.50198(8)	0.00807(7)	0.0312(2)	0.00628(17)	0.781(7)
V(3)	0.4979(4)	-0.0080(3)	-0.0301(10)	0.0133(8)	0.219(7)
P(1)	0.37115(4)	0.62328(4)	0.7487(4)	0.00958(13)	1
P(2)	0.13494(4)	0.37681(4)	0.7523(4)	0.00960(13)	1
P(3)	0.37220(4)	0.37003(4)	0.2537(4)	0.01018(14)	1
P(4)	0.12316(4)	0.63651(4)	0.2512(4)	0.00770(12)	1
Na(1)	0.87260(7)	0.13490(8)	0.7505(7)	0.0152(3)	0.963(3)
Na(2)	0.74731(16)	0.02130(16)	0.4856(4)	0.0242(6)	1
Na(3)	0.13901(13)	0.11865(14)	0.7552(10)	0.0159(5)	0.577(4)
Na(4)	0.36202(9)	0.11525(10)	0.2525(9)	0.0192(4)	0.778(4)
Na(5)	0.49124(8)	0.24769(19)	0.4959(4)	0.0304(4)	1
Na(6)	0.02706(8)	0.24976(19)	0.5019(4)	0.0236(6)	1
Na(7)	0.71553(9)	0.2507(2)	0.5011(4)	0.0245(4)	0.909(4)
Na(8)	0.2502(5)	0.2227(6)	-0.0024(9)	0.027(2)	0.397(15)
Na(9)	0.74803(17)	0.02164(17)	0.0185(5)	0.0244(6)	0.966(7)
Na(10)	0.2518(4)	0.2253(7)	0.5100(10)	0.029(2)	0.411(18)
O(1)	0.00357(10)	0.54510(12)	0.7508(5)	0.0127(4)	1
O(2)	0.22106(10)	0.65074(13)	0.2518(6)	0.0160(4)	1
O(3)	0.1014(2)	0.5794(3)	0.0704(5)	0.0121(8)	1
O(4)	0.0837(2)	0.4027(3)	0.5697(5)	0.0120(8)	1
O(5)	0.1008(2)	0.5797(3)	0.4333(5)	0.0113(8)	1
O(6)	0.27234(10)	0.63310(12)	0.7481(6)	0.0148(4)	1
O(7)	0.0828(2)	0.4020(3)	0.9335(5)	0.0141(9)	1
O(8)	0.42419(19)	0.3961(2)	0.4330(5)	0.0145(7)	1
O(9)	0.42350(19)	0.3995(2)	0.0715(5)	0.0140(7)	1
O(10)	0.36525(14)	0.26755(11)	0.2465(7)	0.0215(5)	1
O(11)	0.3961(2)	0.5669(2)	0.5730(4)	0.0146(7)	1
O(12)	0.07272(12)	0.72438(11)	0.2528(6)	0.0152(4)	1
O(13)	0.28355(11)	0.41486(14)	0.2545(7)	0.0201(5)	1
O(14)	0.3948(2)	0.5692(2)	0.9319(4)	0.0154(8)	1
O(15)	0.14428(16)	0.27418(12)	0.7512(7)	0.0250(6)	1
O(16)	0.41229(12)	0.71592(12)	0.7499(7)	0.0193(5)	1
O(17)	0.50660(10)	0.04849(12)	0.2496(5)	0.0114(4)	1
O(18)	0.22153(12)	0.42436(17)	0.7534(7)	0.0264(6)	1

Table 5
Selected interatomic distances (Å) for Na₄VO(PO₄)₂

Atom–atom	Distance	Atom–atom	Distance	Atom–atom	Distance
V(1)–O(1)	1.882(3)	P(3)–O(13)	1.5222(19)	Na(5)–O(16)	2.368(5)
V(1)–O(1)	1.871(3)	P(4)–O(2)	1.5266(17)	Na(6)–O(4)	2.480(5)
V(1)–O(3)	2.027(4)	P(4)–O(3)	1.561(4)	Na(6)–O(7)	2.458(5)
V(1)–O(4)	1.994(4)	P(4)–O(5)	1.568(4)	Na(6)–O(12)	2.370(4)
V(1)–O(5)	2.006(4)	P(4)–O(12)	1.5193(18)	Na(6)–O(12)	2.358(4)
V(1)–O(7)	1.997(4)	Na(1)–O(1)	2.3313(19)	Na(6)–O(15)	2.542(4)
V(2)–V(3)	0.496(7)	Na(1)–O(3)	2.422(6)	Na(6)–O(15)	2.547(4)
V(2)–O(8)	1.985(3)	Na(1)–O(5)	2.405(6)	Na(7)–O(2)	2.487(4)
V(2)–O(9)	2.000(3)	Na(1)–O(6)	2.2387(19)	Na(7)–O(2)	2.493(4)
V(2)–O(11)	2.000(3)	Na(1)–O(12)	2.253(2)	Na(7)–O(6)	2.481(5)
V(2)–O(14)	1.962(3)	Na(2)–O(2)	2.572(4)	Na(7)–O(6)	2.465(5)
V(2)–O(17)	1.645(4)	Na(2)–O(5)	2.527(4)	Na(7)–O(16)	2.691(4)
V(2)–O(17)	2.149(4)	Na(2)–O(6)	2.496(4)	Na(7)–O(16)	2.684(4)
V(3)–O(8)	2.030(6)	Na(2)–O(11)	2.395(4)	Na(8)–O(10)	2.577(8)
V(3)–O(9)	1.967(6)	Na(2)–O(13)	2.312(5)	Na(8)–O(10)	2.505(8)
V(3)–O(11)	1.939(7)	Na(2)–O(18)	2.413(6)	Na(8)–O(13)	2.708(9)
V(3)–O(14)	2.032(6)	Na(3)–O(1)	2.458(3)	Na(8)–O(15)	2.499(8)
V(3)–O(17)	2.136(7)	Na(3)–O(4)	2.385(7)	Na(8)–O(15)	2.416(8)
V(3)–O(17)	1.658(8)	Na(3)–O(7)	2.435(7)	Na(8)–O(18)	2.859(9)
P(1)–O(6)	1.5329(17)	Na(3)–O(13)	2.287(3)	Na(9)–O(2)	2.564(4)
P(1)–O(11)	1.538(4)	Na(3)–O(15)	2.310(3)	Na(9)–O(3)	2.504(4)
P(1)–O(14)	1.557(4)	Na(4)–O(8)	2.442(7)	Na(9)–O(6)	2.535(5)
P(1)–O(16)	1.5151(19)	Na(4)–O(9)	2.439(7)	Na(9)–O(13)	2.342(5)
P(2)–O(4)	1.553(4)	Na(4)–O(10)	2.262(2)	Na(9)–O(14)	2.394(4)
P(2)–O(7)	1.550(4)	Na(4)–O(17)	2.443(2)	Na(9)–O(18)	2.400(5)
P(2)–O(15)	1.5304(19)	Na(4)–O(18)	2.248(2)	Na(10)–O(2)	2.622(8)
P(2)–O(18)	1.512(2)	Na(5)–O(8)	2.474(4)	Na(10)–O(10)	2.414(8)
P(3)–O(8)	1.541(4)	Na(5)–O(9)	2.480(4)	Na(10)–O(13)	2.740(10)
P(3)–O(9)	1.565(4)	Na(5)–O(10)	2.632(4)	Na(10)–O(15)	2.478(8)
P(3)–O(10)	1.5260(18)	Na(5)–O(10)	2.631(4)	Na(10)–O(15)	2.459(8)
		Na(5)–O(16)	2.342(4)	Na(10)–O(19)	2.897(10)

V(2,3)O₆ octahedra. There are two partially occupied vanadium positions (82% and 18%) separated by 0.496(7) Å inside each octahedron (Fig. 3b). The difference in the occupancies of the V(2) and V(3) positions will be discussed below. Both positions have similar coordination environment, so that we can consider only one of them, namely V(2). Four oxygen atoms, O(8), O(9), O(11) and O(14), form the square plane with the V(2)–O separations of 1.962(3)–2.000(3) Å. Vanadium atom is shifted from the center of the octahedron toward the apical O(17) atom. As a consequence, one short (1.645(4) Å) and one elongated (2.149(4) Å) distances appear. Such situation is typical for the V⁺⁴ or V⁺⁵ ions, which often form vanadyl bonds. Phosphate groups are slightly distorted with the P–O separations being in the range 1.512(2)–1.565(4) Å.

Similar to the other Na_{4+x}VO(PO₄)₂ compounds, two groups of the NaO_n polyhedra can be distinguished in the γ-Na₄VO(PO₄)₂ structure (Fig. 4). The first group contains isolated polyhedra: highly distorted square pyramids for the Na(1), Na(3) and Na(4) atoms and octahedra for the Na(2) and Na(9) atoms. Another group contains polyhedra for the Na(5), Na(6), Na(7), Na(8) and Na(10) atoms.

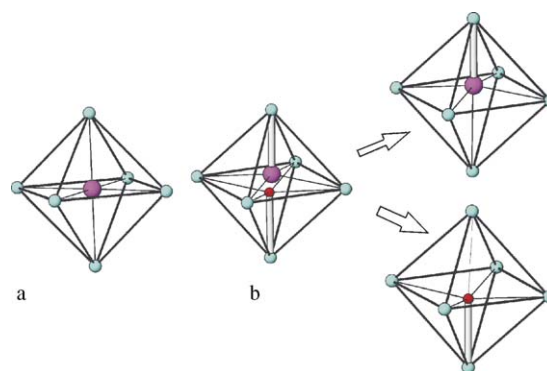


Fig. 3. Two types of octahedra in the structure of γ-Na₄VO(PO₄)₂. Two close vanadium positions in the second polyhedron indicate other possibilities for ordering.

Coordination environments of the Na(5) and Na(6) atoms are almost identical. These sodium atoms are situated in the distorted octahedra forming the infinite chains by sharing the O(10)–O(16) or O(12)–O(15) edges of the Na(5) and Na(6) polyhedra, respectively. The Na(7) atoms are situated in the trigonal prisms that share their triangular faces thus forming triangle channels similar to the Na(5) or Na(6) positions in the Na_{4.35}VO(PO₄)₂ structure. Randomly occupied Na(8) and Na(10) positions are very close

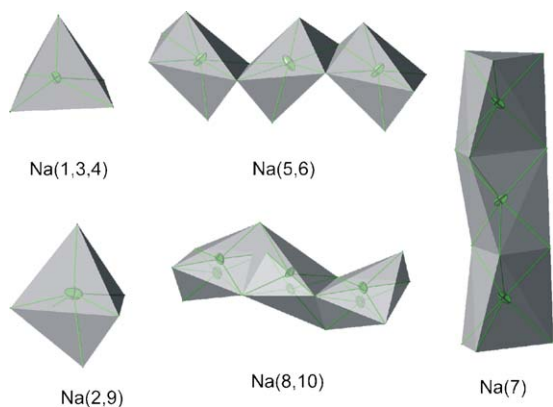


Fig. 4. Coordination polyhedra of the Na atoms and their connections in γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$.

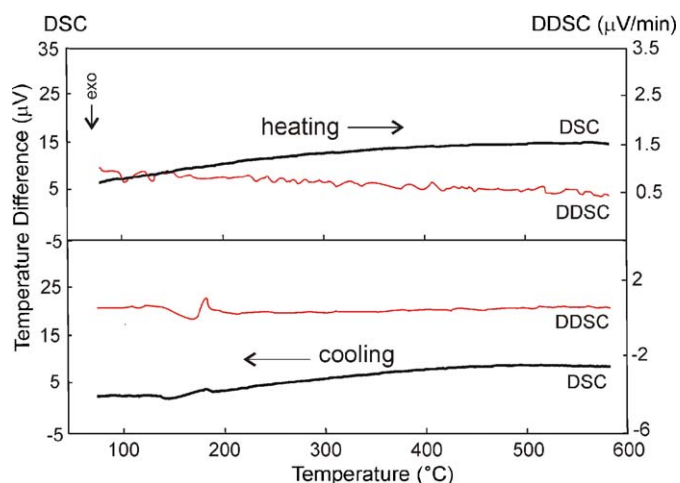


Fig. 5. Heating and cooling DCS curves for the γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ sample.

and separated only by 0.777(14) Å. Therefore, it is reasonable to consider coordination of these atoms together. They are located above and below the square basis of the highly distorted octahedra. The $\text{Na}(8,10)\text{O}_6$ octahedra are linked by common $\text{O}(13)\text{--O}(15)\text{--O}(10)$ faces resulting in zigzag-like channels.

The γ -modification is metastable at ambient conditions. Fig. 5 demonstrates the results of thermal cycling for the sample containing about 95% of γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$. The peak corresponding to the $\alpha \leftrightarrow \beta$ transition [1] around 190 °C is absent on the heating curve. However, this peak appears on the cooling curve and remains during further thermal cycling. The resulting sample cooled after the first cycle contained only green colored low-temperature β -form of $\text{Na}_4\text{VO}(\text{PO}_4)_2$. A thermal cycling of the $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ phase revealed no any peaks corresponding to phase transition.

4. Discussion

An existence of different superstructures for $\text{Na}_4\text{VO}(\text{PO}_4)_2$ has been shown by us earlier [1]. Based on

similarities between this and the isotypical ionic conductor $\text{Na}_4\text{TiO}(\text{PO}_4)_2$, we suggested that the likely origin of the superstructure must be an ordering in the sodium sublattice. Indeed, this is in a good agreement with our results of the crystal structure refinements. Both $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ and γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ structures demonstrate different distribution of sodium atoms in the unit cell. For β - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ we observed completely ordered structure, whereas two structures reported in this work revealed only partially ordered sodium atoms distributions.

In the Ti-containing compounds all superstructures were attributed only to the rearrangement of sodium atoms within the unit cell. In contrast to the latter structures the variety of structural transformations in $\text{Na}_{4+x}\text{VO}(\text{PO}_4)_2$ can be caused by additional factors, for instance, by the presence of vanadyl bonds and their different orientations along the chains. Thus, vanadyl bonds are orderly directed along the chains in the β -modification, while their random distribution is most likely in the α -form. In fact, the situation is even more complicated. The structure can tolerate an excess of sodium atoms accompanied by a change in the vanadium oxidation state. The overstoichiometric sodium content was observed, for example, in $\text{Na}_{4.5}\text{FeO}_{0.5}\text{F}_{0.5}(\text{PO}_4)_2$ [8]. In the latter case, however, the oxygen–fluorine statistics corresponds to the Fe^{3+} ions. On the other hand, the vanadium atom can easily change its oxidation state and form the mixed-valence compounds with partially oxidized or reduced $V_V = +(4 \pm \delta)$. The oxidation state of the vanadium atom has dramatic influence on its coordination (and V–O distances, respectively) which strongly depends on a valence state. So, octahedron can be realized for any oxidation state in a range of $(+3)\text{--}(+5)$. However, there are some differences. So, short vanadyl bond is formed for V^{+4} (with a few exceptions) and V^{+5} (always) when vanadium atom has octahedral coordination. A formation of the vanadyl bond is accompanied by a shift of the vanadium atom from the square base of the octahedra toward one (vanadyl) oxygen atom while the opposite V–O distance becomes elongated. The exceptional regular octahedra $V^{+4}\text{O}_6$ were found only in the perovskite-like structures and newer in chain-containing ones. In contrast to V^{+4} cation the V^{+3} one always has regular (or slightly distorted) octahedral coordination (see for instance, [9–11]).

It is worthwhile to compare the chains in the parent structure of β - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ with those found in the structures determined in this study (Fig. 6). In $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ the average oxidation state of the vanadium atom (+3.65) is lower than that in the parent compound. The decrease in the oxidation state leads to a change in the coordination polyhedra for vanadium atom that now looks as a typical for trivalent vanadium. In this case the vanadium is situated in the center of the octahedron with no vanadyl bonds formed. A calculation of the bond valence sum (BVS) gives the value of 3.75 [11,12] that indirectly supports our conclusion about the decrease in the V oxidation state. One should take into account that the

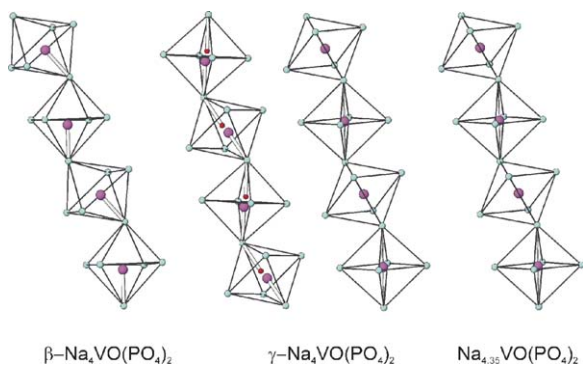


Fig. 6. Chains of the VO_6 octahedra in the β - and γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ and $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ crystal structures.

calculated valence in this case is slightly overestimated since the experimental data were collected at low temperature. Another indirect confirmation for the V oxidation state decrease is the fact that no regular octahedra without vanadyl bond were found among the variety of the V^{+4} compounds containing chain-like structures. Such V^{+4}O_6 octahedra exist only in the perovskite-like compounds that belong to the Ruddlesden–Popper series [13,14]. On the other hand, the chains of regular corner-sharing V^{+3}O_6 octahedra do exist, for example, in $\text{V}(\text{PO}_4)(\text{H}_2\text{O})$ [15] or in $\text{CdV}_2\text{O}(\text{PO}_4)_2$ [16]. Similar transformation of the VO_6 octahedra accompanied by disappearance of the vanadyl bond was observed [17] as a result of lithium intercalation into the V_6O_{13} framework.

The γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ is a new modification of sodium vanadylphosphate. Two types of chains and three different vanadium positions present in this structure. As a consequence, the unit cell symmetry is decreased to $Pbc2_1$ ($Pbca$ for β -modification). Note that three transition metal positions also exist in one of the $\text{Na}_4\text{TiO}(\text{PO}_4)_2$ modifications but all of them belong to the same chain [5]. In γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ the $\text{V}(1)\text{O}_6$ octahedra are of the same type as those found in the $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ structure. The BVS calculation gives the value of 3.75 for this position. The $\text{V}(2)$ and $\text{V}(3)$ positions are shifted from the center of the VO_6 octahedra pointing to the formation of the vanadyl bond. The different occupancies for these two neighboring vanadium positions (overall occupancy is 100%) indicate the preferred orientation of the vanadyl bonds in one direction and, therefore, represent an indirect evidence for further ordering which should result in an increase of the unit cell. Similar nonequivalent filling of the vanadium positions inside the V^{+4}O_6 octahedra was observed in the $\text{Sr}_2\text{VO}(\text{VO}_4)_2$ and $\text{Sr}_2\text{VO}(\text{PO}_4)_2$ structures using single crystal refinement [18] and in the $\text{Li}_4\text{VO}(\text{AsO}_4)_2$ structure solved from X-ray powder diffraction data [19]. The BVS calculation results in oxidation state of +4.15 for the V atoms in these positions.

Thus, we got a different coordination for vanadium atoms in the γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ structure. This difference can be explained taking into account distinctions between crystallochemistry of vanadium in different oxidation

states. One can suggest that a separation of the chains inside the γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ structure is caused by a reordering of the sodium atoms followed by a partial charge redistribution between the V atoms in different chains. As a result, one chain type contains octahedra centered with partially reduced $\text{V}^{+(4-\delta)}$, whereas the $\text{V}^{+(4+\delta)}$ cations form short vanadyl bond typical for $+4 \leq V \leq +5$ and are shifted from the square plane toward the vanadyl oxygen atom. A simultaneous presence of the V^{+3} and V^{+5} ions in the same structure is not common due to possible co-proportionation of these ions resulting in V^{+4} . Therefore, tri- and pentavalent vanadium atoms must be separated in the structure like it occurs in $\text{Ba}_8\text{V}_7\text{O}_{22}$, where the V^{+3} and V^{+5} slabs are separated by the V^{+4} ones [20]. The chains of octahedra in $\text{Na}_4\text{VO}(\text{PO}_4)_2$ are isolated and no direct linkage between polyhedra containing the $\text{V}^{+(4-\delta)}$ and $\text{V}^{+(4+\delta)}$ cations exists. This makes possible a dis-proportionation and an appearance of such an unusual superstructure. Of course, a charge redistribution in the γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ structure looks very unusually, nevertheless there are some other indications for that. So, β - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ is green colored whereas γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ and $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ are dark gray. Furthermore, a thermal treatment of the γ -modification results in a formation of a single phase green β -form. Such behavior indicates different charge state of the vanadium atoms in two modifications of $\text{Na}_4\text{VO}(\text{PO}_4)_2$.

More illustrative confirmation of the charge re-distribution inside the γ - $\text{Na}_4\text{VO}(\text{PO}_4)_2$ structure may be obtained by analyzing the M–O bond valence (BV) for the closest cationic neighbors of the oxygen atom shared between two VO_6 octahedra (Table 6). The change in the vanadium oxidation number should be accompanied by change of the M–O bond lengths while keeping the BVS of the oxygen atom as a constant (~ 2.0) according to the second Pauling rule. Thus, a decrease in the vanadium oxidation state

Table 6

Distances (Å) and calculated bond valences (BV) between the V and Na atoms and oxygen atom shared by neighboring VO_6 octahedra in chains in the $\text{Na}_{4+x}\text{VO}(\text{PO}_4)_2$ structures

M–O	$\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ $V_V = 3.65$	$\text{Na}_4\text{VO}(\text{PO}_4)_2$		
		γ -form $V_V = 4-\delta$	γ -form $V_V = 4+\delta$	β -form $V_V = 4.0$
Na–O	2.328	2.331	2.443	2.468
BV	0.244	0.241	0.176	0.166
Na–O	2.355	2.458	3.432	2.879
BV	0.223	0.170	0.012	0.055
$\Sigma(\text{BV})$ for Na	0.467	0.411	0.188	0.221
V–O	1.875	1.882	1.645	1.637
BV	0.782	0.767	1.440	1.488
V–O	1.875	1.871	2.148	2.160
BV	0.782	0.790	0.377	0.362
$\Sigma(\text{BV})$ for V	1.546	1.557	1.817	1.850
$\Sigma(\text{BV})$ for O	2.013	1.968	2.005	2.071

$\Sigma(\text{BV})$ means the bond valence sum for Na or V cations with bridging oxygen atom.

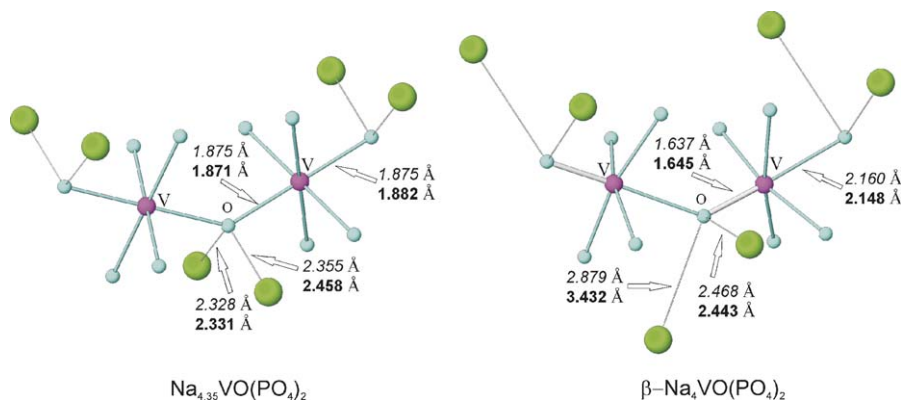


Fig. 7. The shortest M–O distances for oxygen atom shared between two neighboring VO_6 octahedra in the $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ and $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$ structures. Corresponding distances in $\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$ are printed in bold.

should stimulate the shortening of the Na–O distances (increase of the BV) to compensate for elongation of the V–O bonds. On the other hand, an increase of the vanadium oxidation state will cause the opposite effect. Two fragments of the $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$ and $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$ structures illustrating the data in Table 6 are shown in Fig. 7. One can see that the Na–O distances and, consequently, the corresponding BVS for the chain of the $\text{V}^{+(4-\delta)}\text{O}_6$ octahedra in the $\gamma\text{-Na}_4\text{VO}(\text{PO}_4)_2$ structure are practically the same as those for the chain of the $\text{V}^{+3.72}\text{O}_6$ octahedra found in $\text{Na}_{4.35}\text{VO}(\text{PO}_4)_2$. An appearance of the short vanadyl bond inside the V^{+4}O_6 octahedra in the $\beta\text{-Na}_4\text{VO}(\text{PO}_4)_2$ structure results in nonequivalent increase of the Na–O distances (2.468 and 2.879 Å) and in decrease of the BV of Na–O. Further increase in the oxidation state of the vanadium situated in the $\text{V}^{+(4+\delta)}\text{O}_6$ octahedra (γ -phase) causes an elongation of one of two Na–O distances up to a non-bonding value (3.432 Å). Therefore, it may be concluded that the distribution of sodium atoms between the chains in the $\text{Na}_4\text{VO}(\text{PO}_4)_2$ structure is a major reason for the charge redistribution between vanadium atoms located in different chains. Evidently, these BV calculations provide only estimates due to the presence of randomly occupied Na and V positions. Nevertheless, the BVS analysis allows to assume the structural reasons for charge re-distribution between the V atoms in neighboring chains.

5. Conclusions

The variety of structural transformations for the $\text{Na}_{4+\delta}\text{VO}(\text{PO}_4)_2$ compound is caused by several major factors:

- a distribution of sodium atoms between the chains with full or partial ordering;
- a presence of the vanadyl bond that may be oriented in different ways;
- a possibility of the vanadium atom to change its oxidation state that may be caused by a change in sodium content and results in different coordination environment.

Acknowledgments

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Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at: [doi:10.1016/j.jssc.2006.05.013](https://doi.org/10.1016/j.jssc.2006.05.013).

References

- [1] R.V. Panin, R.V. Shpanchenko, A.V. Mironov, Yu.A. Velikodnyi, E.V. Antipov, J. Hadermann, E.E. Kaul, C. Geibel, *Chem. Mater.* 16 (2004) 1048.
- [2] B.A. Maximov, N.E. Klokova, I.A. Verin, V.A. Timofeeva, *Kristallografiya (Russia)* 35 (1990) 847.
- [3] N.E. Klokova, B.A. Maximov, R.A. Tamazyan, *Kristallografiya (Russia)* 38 (1993) 56.
- [4] R.A. Tamazyan, B.A. Maximov, N.B. Bolotina, N.E. Novikova, V.I. Simanov, *Kristallografiya (Russia)* 39 (1994) 478.
- [5] N.B. Bolotina, B.A. Maximov, V. Petricek, V.I. Simanov, *Kristallografiya (Russia)* 40 (1995) 611.
- [6] B.A. Maximov, N.B. Bolotina, V.I. Simonov, V. Petricek, H. Schulz, *Acta Crystallogr. B* 50 (1994) 261.
- [7] V. Petricek, M. Dusek, *The Crystallographic Computing System JANA2000*, Institute of Physics, Praha, Czech Republic, 2000.
- [8] B.A. Maximov, N.B. Bolotina, R.A. Tamazyan, *Z. Kristallogr.* 209 (1994) 649.
- [9] P.Y. Zavalij, M.S. Whittingham, *Acta Crystallogr. B* 55 (1999) 627.
- [10] S. Boudin, A. Guesdon, A. Leclaire, M.-M. Borel, *Int. J. Inorg. Mater.* 2 (2000) 561.
- [11] M. Schindler, F.C. Hawthorne, W.H. Baur, *Chem. Mater.* 12 (2000) 1248.
- [12] I.D. Brown, D. Altermatt, *Acta Crystallogr. B* 41 (1985) 244.
- [13] M.J. Rey, P. Dehaut, J.C. Joubert, B. Lambert-Andron, M. Cyrot, F. Lackmann, *J. Solid State Chem.* 86 (1990) 101.
- [14] J. Garcia-Jaca, J.L. Mesa, M. Insausti, J.I.R. Larramendi, M.I. Arriortua, T. Rojo, *Mater. Res. Bull.* 34 (1999) 289.

- [15] A. El Badraoui, J.Y. Pivan, M. Maunaye, O. Pena, M. Louer, D. Louer, *Ann. Chim. (Paris)* 23 (1998) 97.
- [16] S. Boudin, A. Grandin, M.M. Borel, A. Leclaire, B. Raveau, *J. Solid State Chem.* 111 (1994) 380.
- [17] Ö. Bergström, T. Gustafsson, J.O. Thomas, *Acta Crystallogr. C* 53 (1997) 528.
- [18] R.V. Shpanchenko, J. Hadermann, Private communication.
- [19] M.A.G. Aranda, J.P. Attfield, S. Bruque, M. Martinez-Lara, *Inorg. Chem.* 31 (1992) 1045.
- [20] G. Liu, J.E. Greedan, *J. Solid State Chem.* 108 (1994) 371.