SUPPLEMENTARY INFORMATION

Rubidium vanadium(III) vanadyl(IV) phosphate, $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$: crystal chemistry and low-dimensional magnetism

Olga Yakubovich,[*a] Galina Kiriukhina,[a,b] Anatoliy Volkov,[c] Olga Dimitrova,[a] Ratibor Chumakov,[d] Larisa Shvanskaya,[a,e] and Alexander Vasiliev[*a,e]

[a]*Lomonosov Moscow State University, Moscow 119991.*
[b]*Korzhinskii Institute of Experimental Mineralogy RAS, 142432 Chernogolovka, Russia.*
[c]*Skolkovo Institute of Science and Technology, Moscow 121205, Russia.*
[d]*National Research Centre "Kurchatov Institute", Moscow 123182, Russia*
[e]*National University of Science and Technology MISIS, Moscow 119049, Russia*
*corresponding authors: yakubovich.olga320@gmail.com, anvas2000@yahoo.com

1. X-Ray diffraction data

Table S1. $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$. Selected geometric parameters (Å)

Rb1—O19[i]	2.876 (14)	Rb6—O9	3.591 (13)
Rb1—O21[i]	2.899 (13)	Rb6—O25	3.636 (14)
Rb1—O22	2.940 (12)	V1—O17	1.973 (13)
Rb1—O12	2.994 (13)	V1—O9[iii]	1.976 (12)
Rb1—O6[i]	3.036 (12)	V1—O12[x]	1.983 (13)
Rb1—O4[i]	3.070 (13)	V1—O5[xii]	2.010 (13)
Rb1—O9[ii]	3.129 (12)	V1—O26[x]	2.079 (12)
Rb1—O15	3.131 (13)	V1—O15[x]	2.097 (12)
Rb2—O23[iii]	2.947 (13)	V2—O14	1.976 (12)
Rb2—O13[iv]	2.959 (13)	V2—O1	1.982 (13)
Rb2—O16[v]	2.967 (13)	V2—O4[iv]	2.003 (13)
Rb2—O26[vi]	2.975 (12)	V2—O7[iv]	2.030 (13)
Rb2—O3	2.977 (12)	V2—O6[iv]	2.057 (12)
Rb2—O5[v]	2.977 (13)	V2—O13[iv]	2.082 (12)
Rb2—O1	3.004 (13)	V3—O22	1.588 (13)
Rb2—O20[vii]	3.177 (14)	V3—O10	1.931 (12)
Rb3—O16	2.836 (12)	V3—O3	1.946 (11)
Rb3—O8[viii]	2.967 (12)	V3—O18	1.969 (12)
Rb3—O23[viii]	3.004 (13)	V3—O11[iv]	2.000 (12)
Rb3—O13[viii]	3.048 (12)	V4—O23	1.618 (12)
Rb3—O17[vii]	3.053 (12)	V4—O24	1.923 (14)

Rb3—O23^{ix}	3.067 (13)	V4—O25^{xi}	1.937 (13)
Rb3—O10^{vii}	3.138 (12)	V4—O8	1.982 (13)
Rb4—O14	2.855 (13)	V4—O2^{ix}	1.984 (12)
Rb4—O20^{vii}	2.889 (12)	P1—O3	1.506 (12)
Rb4—O6	2.962 (12)	P1—O7	1.521 (13)
Rb4—O22^{iv}	2.978 (12)	P1—O1	1.525 (12)
Rb4—O1	3.039 (13)	P1—O19	1.545 (13)
Rb4—O11^{ix}	3.212 (12)	P2—O4	1.526 (13)
Rb4—O2	3.247 (13)	P2—O9	1.533 (12)
Rb4—O24^{ix}	3.252 (13)	P2—O8	1.535 (13)
Rb4—O7^{iv}	3.301 (13)	P2—O21	1.565 (12)
Rb5—O19^{vi}	2.957 (12)	P3—O17	1.512 (13)
Rb5—O26	2.980 (13)	P3—O10	1.517 (12)
Rb5—O8^{iii}	3.067 (13)	P3—O20	1.529 (13)
Rb5—O25^{vi}	3.081 (13)	P3—O12	1.532 (13)
Rb5—O9^{iii}	3.150 (13)	P4—O2	1.501 (12)
Rb5—O17	3.163 (14)	P4—O5	1.513 (13)
Rb5—O18^{vi}	3.181 (12)	P4—O14	1.523 (13)
Rb5—O12^{x}	3.229 (12)	P4—O16	1.532 (12)
Rb5—O10	3.282 (12)	P5—O11	1.525 (12)
Rb6—O7	2.837 (12)	P5—O6	1.534 (13)
Rb6—O21^{xi}	2.922 (13)	P5—O13	1.548 (13)
Rb6—O15^{ii}	3.034 (12)	P5—O24	1.554 (13)
Rb6—O4	3.041 (13)	P6—O25	1.520 (13)
Rb6—O14^{iv}	3.214 (12)	P6—O18	1.525 (12)
Rb6—O2^{iv}	3.313 (12)	P6—O15	1.528 (13)
Rb6—O18	3.441 (13)	P6—O26	1.538 (13)
Rb6—O22	3.505 (13)		

Symmetry code(s): (i) $x+1, y, z$; (ii) $-x+1, -y+2, -z+1$; (iii) $x+1, y, z+1$; (iv) $-x, -y+1, -z+1$; (v) $-x, -y+1, -z+2$; (vi) $-x+1, -y+2, -z+2$; (vii) $x-1, y, z$; (viii) $x, y, z+1$; (ix) $-x-1, -y+1, -z+1$; (x) $-x+2, -y+2, -z+2$; (xi) $-x, -y+2, -z+1$; (xii) $-x+1, -y+1, -z+2$.

Table S2. $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$. Bond valence data

Atom	P1	P2	P3	P4	P5	P6	V1	V2	V3	V4	Rb1	Rb2	Rb3	Rb4	Rb5	Rb6	Σ
O1	1.28							0.58				0.13		0.12			2.11
O2			1.37							0.58				0.07		0.06	2.08
O3	1.35								0.65			0.15					2.15
O4		1.28						0.49			0.11					0.12	2.00
O5			1.32				0.49					0.15					1.96
O6				1.25				0.43			0.12			0.15			1.95
O7	1.30							0.46						0.06		0.21	2.03
O8		1.25								0.59			0.15		0.11		2.10
O9		1.26						0.53			0.10				0.09	0.03	2.01
O10			1.31						0.67				0.09		0.06		2.13
O11				1.28					0.56					0.08			1.92
O12		1.25						0.52			0.14				0.07		1.98
O13				1.21				0.40				0.15	0.12				1.88
O14			1.29					0.63						0.20		0.08	2.20
O15						1.27	0.38					0.09				0.13	1.87
O16/OH			1.25									0.15	0.21				**1.61**
O17		1.33						0.54					0.12		0.09		2.08
O18						1.28			0.60						0.08	0.04	2.00
O19/OH	1.21										0.19				0.15		**1.55**
O20/OH			1.26									0.08		0.18			**1.52**
O21/OH		1.15									0.18					0.17	**1.50**
O22										1.70	0.16			0.14		0.04	2.04
O23										1.56		0.16	0.11;0.14				1.97
O24					1.18					0.69				0.07			1.94
O25						1.30				0.66					0.11	0.02	2.09
O26						1.24	0.40					0.14			0.14		1.92
Σ	5.14	4.94	5.15	5.20	4.92	5.09	2.86	2.99	4.18	4.08	1.08	1.11	0.94	1.07	0.90	0.90	

1. XPS - data
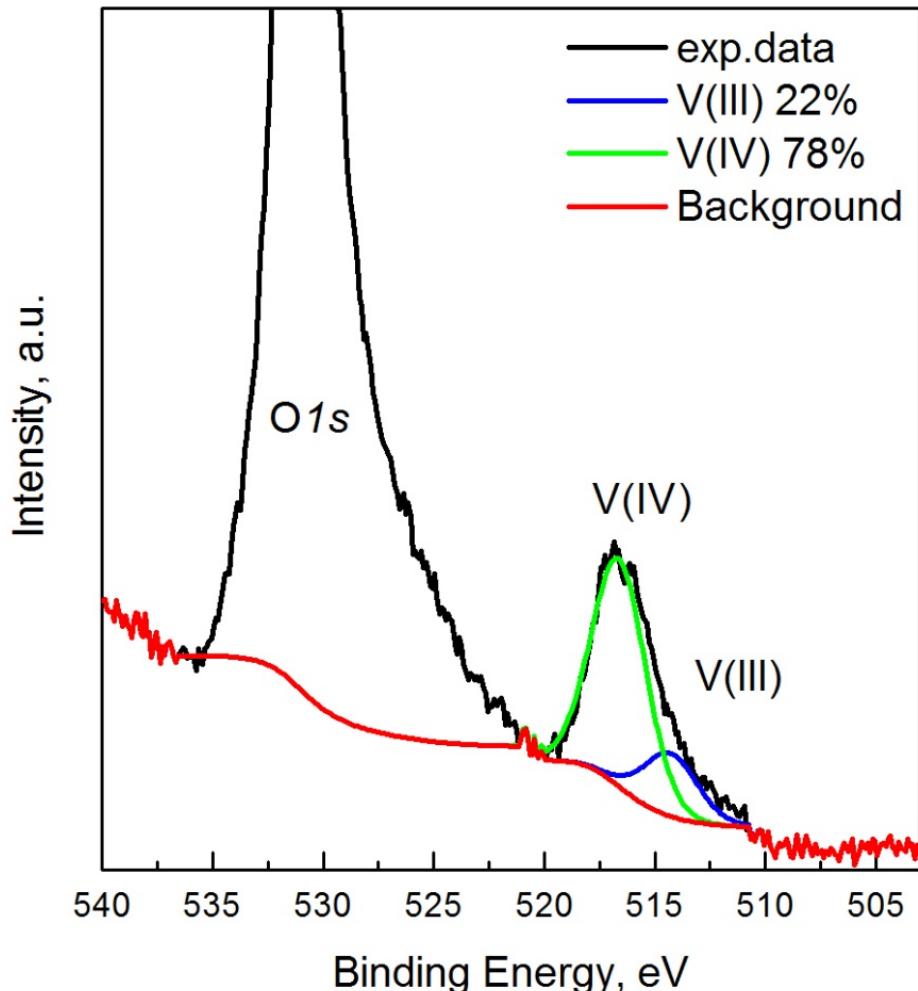
Figure S1. V 2p (and O 1s) spectra of $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$.

As can be seen from Fig. S1, the vanadium spectrum in $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$ contains two peaks corresponding to V(III) and V(IV). The vanadium ions' concentrations differ from the bulk value, which is a standard feature of the XPS method, where the analysis depth is limited to 10 nm, and the sample surface tends to be further oxidized under atmospheric conditions. Thus, XPS study confirmed the presence of vanadium ions in 3+ and 4+ oxidation states.

2. FTIR spectroscopy

The FTIR spectrum (Fig. S2) shows a complex spectral profile with a series of overlapping bands. Two broad band systems are present in the range of about 3300 cm^{-1}, from 1400 to 700 cm^{-1} and a third band system from 650 to 500 cm^{-1}.
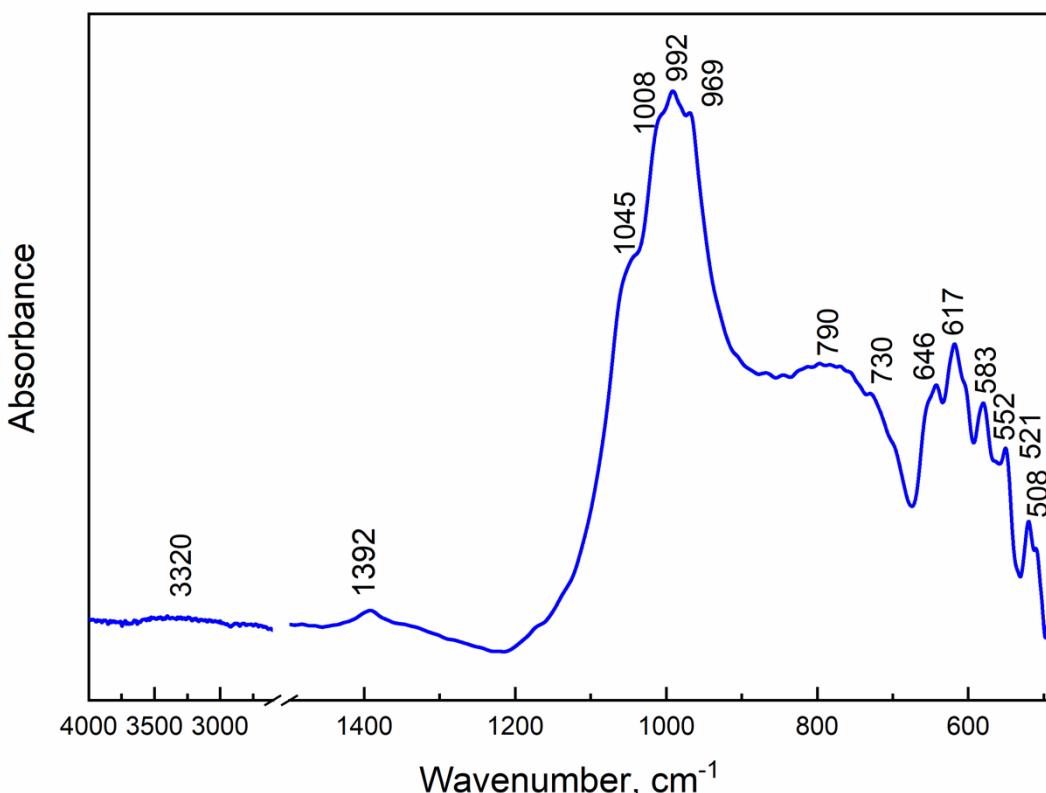
Fig. S2. FTIR spectrum of $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$.

As shown in Fig. S2, in the region of stretching vibrations of OH groups, 3000–3500 cm^{-1}, there is a broad weak band at 3320 cm^{-1} in $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$. The low intensity of this band and its broadening can be attributed to the statistical character and the low amount of H atoms taking in account the similar energies of hydrogen bonds.

The second wide region, from 1400 to 700 cm^{-1}, features weak absorption band at 1392 cm^{-1}. This band is typical of stretching vibrations of OH groups with a low degree of O-H bond covalence as in the case of acid salts.[1] Recently, it was established, that if the VO^{2+} group is coordinated by phosphates, the value of the typical V=O stretching motion is found at about 990 cm^{-1}. Thus the strongest intensity band at 992 cm^{-1} is assigned to the symmetric vibrations of the short terminal V=O bond in $Rb_3V^{3+}(V^{4+}O)(PO_4)(H_{0.5}PO_4)_2$. However, this band can be overlapping to the mode of symmetric stretching vibration of PO_4 group.[3] The band at 969 cm^{-1} could correspond to antisymmetric vibrations of the V=O bond. Antisymmetric stretching vibrations of PO_4 tetrahedra appear at 1045 and 1008 cm^{-1}. The broad band with the maximum at 790 and the shoulder at 730 cm^{-1} are assigned to asymmetrical stretching vibrations of V – O – V bond according.[4-6] The third 650 to 500 cm^{-1} region includes medium intensity bands, which are typical for antisymmetric bending mode of PO_4 groups.[3]

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