

Revisiting hollandites: channels filling by main-group elements together with transition metals in Bi_{2-y}VyV₈O₁₆

Lebedev, O. I.; Hébert, S.; Roddatis, V.; Martin, C.; Turner, S.; Krasheninnikov, A. V.; Grin, Y.; Maignan, A.;

Originally published:

June 2017

Chemistry of Materials 29(2017)13, 5558-5565

DOI: <https://doi.org/10.1021/acs.chemmater.7b00693>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-25690>

Release of the secondary publication
on the basis of the German Copyright Law § 38 Section 4.

Revisiting hollandites:**channels filling by main-group elements together with transition metals****in $\text{Bi}_{2-y}\text{V}_y\text{V}_8\text{O}_{16}$**

O. I. Lebedev¹, S. Hébert¹, V. Roddatis², C. Martin¹, S. Turner³,
A.V. Krasheninnikov^{4,5,6}, Y. Grin⁷, and A. Maignan^{1*}

¹Laboratoire CRISMAT, UMR 6508 CNRS/ENSICAEN/UCBN, 6 bd du
Maréchal Juin, F-14050 CAEN Cedex 4 – France

²Institut für Materialphysik Universität Göttingen, Friedrich-Hund-Platz 1,
37077 Göttingen

³EMAT, Department of Physics, University of Antwerp, B-2020, Antwerp,
Belgium

⁴Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and
Materials Research, 01328 Dresden, Germany

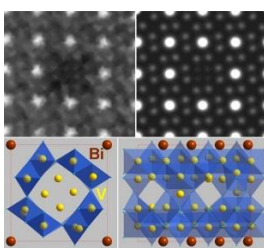
⁵Department of Applied Physics, Aalto University, P.O. Box 1100, 00076
Aalto, Finland

⁶National University of Science and Technology MISiS, 4 Leninskiy prospekt,
Moscow, 119049, Russian Federation

⁷Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40,
01187 Dresden, Germany

Abstract

Starting from the nominal $\text{Bi}_x\text{V}_8\text{O}_{16}$ formula, state-of-the-art transmission electron microscopy investigation has been made to propose the new chemical formula $\text{Bi}_{2-y}\text{V}_y\text{V}_8\text{O}_{16}$ for this hollandite structure. This results from the filling of the channels by main-group elements together with vanadium (V^{5+}) species, with variable content of Bi and V inside the channels. The influence of the Bi content and of this local disorder on the magnetic and transport properties has been investigated in polycrystalline samples of $\text{Bi}_x\text{V}_8\text{O}_{16}$ with nominal composition $x = 1.6$ and $x = 1.8$. The rather x -independent electrical resistivity ($\approx 5 \text{ m}\Omega\cdot\text{cm}$) and Seebeck coefficient at high T ($-35 \mu\text{V}\cdot\text{K}^{-1}$ at 900 K) is discussed in terms of an unchanged V oxidation state resulting from the filling-up of the wide channels with Bi and V. It is proposed that this local disorder hinders the charge/orbital setting below 60 K on the V ions of the V_8O_{16} framework. Hollandites exhibit complex electronic and magnetic properties with potential applications in the field of batteries, photocatalysis or nuclear waste storage, and these results show that a careful and detailed investigation of the nature and content of the cations inside the channels is crucial to better understand the doping and disorder impact on their properties.



*Corresponding Author

Sylvie HEBERT

Laboratoire CRISMAT, ENSICAEN/CNRS, 6 boulevard du Maréchal Juin, 14050

Caen cedex 4 - France

sylvie.hebert@ensicaen.fr

Tel: 33.(0)2.31.45.29.10

Introduction

The hollandite family with the chemical composition $A_xM_8O_{16}$ ($A = K, Pb, Ba, Bi, Ag, \dots$) containing magnetic transition metals (M) with mixed valence exhibit a wide range of interesting physical properties related to electronic correlations, magnetic frustration and orbital ordering¹⁻¹⁴. The M_8O_{16} framework with different kinds of 1D channels allows insertion and release of cations or small molecules in the wider tunnels making hollandites interesting candidates for several applications as electroactive cathode¹⁵, photocatalysis¹⁶⁻¹⁷, or as host material for bearing radioactive ions¹⁸⁻¹⁹.

The building unit of this crystal structure consists of stripes made up of infinitely stacked edge-sharing MO_6 octahedra, which share corners to form a M_8O_{16} framework with wide and narrow tunnels. The average formal oxidation state of M is tetravalent. The wide tunnels are occupied in commensurate or incommensurate manner by A^{n+} cations up to a maximum of $x = 2$ (figure 1b). The charge transfer from the A^{n+} cations to the M_8O_{16} hollandite network generates a M^{3+}/M^{4+} mixed valence for the M species. In the M_8O_{16} network, these extra electrons order in a 1D pattern leading to complex M-M magnetic exchange pathways, with frustration in the M_3 triangles (see Fig. 1c, with $Bi_xV_8O_{16}$ for $x = 1.625$). Through corner sharing oxygen atoms bridging the stripes, there exists an additional magnetic exchange between the zigzag chains along the stripes¹². Moreover, the tetragonal crystal structure is likely to exhibit distortions, and can become monoclinic, with the large tunnels that do not longer have the square shape, or with the Mo_4 "clusters" in $(MoO_6)_2$ stripes⁵. The tetragonal-to-monoclinic transition combined with charge/orbital ordering is responsible for the metal-to-insulator transition (MIT) in $K_2V_8O_{16}$ and $K_2Cr_8O_{16}$ ^{2-3, 14}. The complex properties of these hollandites has stimulated experimental and theoretical investigations to better understand the strong coupling between the lattice, spins and charges¹⁻¹⁴, and the role of the frustration inside the ribbons on magnetism¹²⁻¹³. The defects chemistry inside the channels has also been found to play a major role on the properties such as ionic conductivity²⁰, or on the resistivity of Ru hollandites²¹. The filling mechanism inside the channels of these hollandites needs to be well understood to better analyze the doping effect and possible disorder impact.

Despite all these features, only a moderate activity has been focused on local atomic arrangements in hollandites and their correlation with the properties, applying in particular the state-of-the-art transmission electron microscopy. To the best of our knowledge, only few

reports have been published^{20, 22-24} in the last twenty years. M.L.Carter et al. presented extensive studies on barium titanate $\text{Ba}_x\text{M}_y\text{Ti}_{8-y}\text{O}_{16}$ by electron diffraction and appearance of modulated structures.²²⁻²³ L.Nistor et al reported high resolution transmission electron microscopy and electron diffraction studies of defects in the natural hollandite $\text{Ba}_x\text{Mn}_8\text{O}_{16}$ and found as a main structural feature shear plane defects.²⁴ The different arrangements of these defects were attributed to commensurate and incommensurate modulations in ED patterns. We did not find in the literature results of detailed studies of the reasons for these structural features with atomic resolution.

For vanadium-based hollandites only, a MIT for all of them has been evidenced with a coupled magnetic transition at 180 K for $\text{K}_2\text{V}_8\text{O}_{16}$ ², 140 K for $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$ ¹⁰ and near 60 K for $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$ ⁷. Considering the filling level of the wider tunnel, the formal oxidation state of vanadium is larger than 3.5 for the two first ($\nu_V = 3.75$ and 3.60 for $\text{K}_2\text{V}_8\text{O}_{16}$ and $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$, respectively), but smaller for $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$ with $\nu_V = 3.325$. This correlates with the lower T_{MIT} for the bismuth hollandite. Additionally, the coexistence of a rather constant resistivity at high T (from 300 to 1000 K) together with a continuous increase of $|S|$ up to 1000 K in $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$ motivates a more detailed investigation of physical properties of synthetic hollandites as a function of x. The $\text{Bi}_x\text{V}_8\text{O}_{16}$ bismuth vanadate ($1.6 \leq x \leq 1.8$)^{7, 8, 25-26} is well worth studying for its structural features and their impact on magnetic and transport properties.

In the following, we report the evidence of a simultaneous filling of channels by main-group elements and transition metals in $\text{Bi}_{2-y}\text{V}_y\text{V}_8\text{O}_{16}$ and its possible linking with the physical properties. The crystal structure has been characterized by atomic-resolution transmission electron microscopy. The wider tunnels of the hollandite structure are not only partially occupied by Bi^{3+} but also contain tetrahedrally coordinated vanadium cations, a result which is supported by electronic structure calculations. The vanadium oxidation state determined by EELS and its relation with the Seebeck coefficient is also discussed.

Experimental section

Polycrystalline samples of $\text{Bi}_x\text{V}_8\text{O}_{16}$ with x values in the range of $1.6 \leq x \leq 1.8$ have been synthesized by solid state reaction. According to the nominal composition $\text{Bi}_x\text{V}_8\text{O}_{16}$, stoichiometric amounts of Bi_2O_3 , V_2O_3 and V_2O_5 were mixed in a glove box and pressed in bar-shaped specimen ($2 \times 2 \times 10$ mm). An alumina crucible containing the bars was sealed in a silica tube under primary vacuum. The ampoule was heated at 1000 °C for 12 hours and

1
2
3 subsequently cooled down to room temperature in 6 hrs. The obtained black product was
4 characterized by room temperature (RT) X-ray powder diffraction (XRD, CuK_α radiation) and
5 transmission electron microscopy.
6
7

8
9 Specimens for electron microscopy studies were ground in methanol and drop cast onto
10 a holey carbon film fixed on a 3 mm copper grid. Transmission electron microscopy (TEM)
11 and electron diffraction (ED) studies were performed using FEI Tecnai G2 30 UT microscope
12 operated at 300 kV, with a point resolution of 0.17 nm. High resolution high-angle annular
13 dark-field STEM (HAADF-STEM) experiments were carried out by using an aberration
14 double-corrected JEM ARM200F microscope operated at 200 kV equipped with a
15 CENTURIO EDX detector and GIF Quantum spectrometer. Electron energy-loss
16 spectroscopy experiments (EELS) were performed on Titan “cubed” microscope, equipped
17 with an electron monochromator and a GIF Quantum spectrometer, operated at 120 kV in
18 scanning TEM mode. The monochromator provided an energy resolution of 200 meV. The
19 convergence semi-angle α was 18 mrad, the acceptance inner semi-angle β was 130 mrad.
20 Atomic models for simulation were built using Atoms 6.4, CrystalMaker and the Vesta²⁷
21 software packages. The high resolution HAADF-STEM simulated images were calculated
22 using the QSTEM package²⁸.
23
24
25
26
27
28
29
30
31
32

33
34 Magnetic measurements were performed by SQUID magnetometer. For $T < 325$ K, the
35 four-probe technique and steady-state method were used for electrical resistivity (ρ) and
36 Seebeck (S) coefficient measurements, respectively. Above that temperature, a ULVAC
37 ZEM3 system was used to perform simultaneous measurements of ρ and S in an inert gas
38 atmosphere.
39
40
41
42

43
44 The first-principles calculations were carried out using the Vienna *Ab-initio* Simulation
45 Package (VASP)²⁹⁻³⁰ software on CRAY XC40 supercomputer. We used the generalized
46 gradient approximation with the Perdew-Burke-Ernzerhof³¹ parameterization and the
47 projected augmented wave³² approach to describe core electrons. A rectangular $2 \times 2 \times 4$
48 supercell was used. The larger supercells can hardly be studied with the same accuracy due to
49 computational limitations even on the CRAY XC40 supercomputer.
50
51
52
53
54

55 **Results and discussion**

56 Structure characterization by XRD

57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

X-ray powder diffraction ($x = 1.6$ in Fig. 1a) confirms the hollandite structure with the space group $I4/m$ reported for a $\text{Bi}_{1.625}\text{V}_8\text{O}_{16}$ single crystal²⁵⁻²⁶. The unit cell parameters $a = 9.9323(2)$ Å and $c = 2.9128(1)$ Å ($V = 287.35(1)$ Å³) of the material with the nominal composition $\text{Bi}_{1.6}\text{V}_8\text{O}_{16}$ are close to the previously reported $a = 9.930(4)$ Å and $c = 2.914(1)$ Å ($V = 287.33$ Å³)²⁵⁻²⁶. Increasing the x value up to 1.8 in the starting mixture of precursors slightly increases the unit cell volume with decreasing a parameter and increasing c parameter: $a = 9.9225(2)$ Å, $c = 2.9230(1)$ Å and $V = 287.78(1)$ Å³. No significant impurities were detected in XRD patterns for all samples.

TEM studies

The hollandite-type crystal structure of $\text{Bi}_{1.625}\text{V}_8\text{O}_{16}$ comprises a network of double rutile-like ribbons of edge-sharing VO_6 octahedra sharing corners and forming the wide square channels occupied by Bi^{3+} cations (Fig. 1b).

Figure 2a-b shows the electron diffraction (ED) patterns along the most informative zone axes $[001]^*$, $[100]^*$ and $[111]^*$ for $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$. The ED patterns were completely indexed using the space group $I4/m$ (no. 87) and the unit cell parameters determined by powder XRD. No significant differences were observed in ED pattern for different x values which is in good agreement with the conclusions from powder XRD data. The HRTEM study of $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$ (Fig. 2b) was performed along the most informative $[001]$ zone along wide tunnels. It exhibits uniform contrast, free of any modulation and defects within the single crystallites. No superstructure features resulting from long-range ordering were observed as well. However, a careful analysis of ED patterns (Fig. 2a) revealed the appearance of diffuse streak lines normal to c^* axis and parallel to the $h0l$ spots rows in all $[100]^*$ and $[111]^*$ ED patterns which can be interpreted in terms of short-range ordering of Bi vacancies in the incommensurate structure. A similar behaviour was observed previously in barium titanate hollandites²³ and attributed to A cations ordering along the tunnel direction. In order to shed light on these features the state-of-the-art TEM microscopy was applied. The direct interpretation of HRTEM images of a complex compound with a large unit cell is not always straightforward. The phase-contrast image formation in HRTEM is not very sensitive to small compositional variations within a single atomic column. To overcome these drawbacks, incoherent HAADF-STEM imaging, so called ‘Z-contrast’ was used to clarify the crystal structure model of $\text{Bi}_x\text{V}_8\text{O}_{16}$ and determine possible structural or/and compositional variations at the atomic level. The contrast in HAADF-STEM is roughly proportional to the thickness of the specimen and square atomic

1
2
3 number Z^2 of the components, making it possible to detect even small changes in the
4 composition and positions of Bi ($Z = 83$) or/and V ($Z = 23$).
5

6
7 High resolution HAADF-STEM images of the nominal $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$ structure along [001]
8 and [100] zone axis are shown in Figure 3. The columns of Bi and V atoms can easily be
9 distinguished in the [001] image (Fig. 3a): the brightest square-arranged dots correspond to
10 the Bi atomic columns ($Z = 83$) whereas the eight less bright dots surrounding each Bi atomic
11 column are V atomic columns ($Z = 23$). The same definition applies to [100] HAADF-STEM
12 image (Fig. 3b) where brightest dots correspond to row of Bi atoms and less bright to V atoms
13 in between the layers. Importantly, the Fourier transformation (FT) of the [100] image
14 reproduces diffuse line normal to c^* -axis similar to that of ED pattern (Fig. 2a). A careful
15 inspection of the images reveals the presence of numerous inhomogeneities in the local
16 contrast along both zone axes. The contrast in the vanadium columns does not change
17 markedly over the whole region of the HAADF-STEM image, whereas the contrast in the
18 vicinity of the Bi columns in the wide channels varies strongly. It appears as a complete lack
19 of contrast in [001] image (Fig. 3a) or more frequently as a significant reduction in intensity
20 in both directions (Fig. 3a,b) in comparison with the regular contrast of neighboring Bi atomic
21 columns as we can see from intensity plot profile in Figure 3c. The ‘split’ of the Bi spots in
22 the view along [100] is caused by different orientation of the incommensurate Bi chains
23 (starting coordinates z and $-z$) and shift of the Bi atoms from the tunnel axis. The careful
24 analysis of [100] high resolution HAADF-STEM image (Fig. 3d) also reveals a lack of Bi
25 atoms in the expected positions reflecting their partial occupancy.
26
27
28
29
30
31
32
33
34
35
36
37
38
39

40 In the [001] image (Fig.3a), the contrast within the wide channel (Bi columns) can be
41 absent, as shown by the arrow. Instead, a square arrangement of lower contrast intensity
42 appears displaying contrast similar to the other V columns and suggesting the presence of
43 additional V atoms inside the wide channels (Fig.4b). The filling of channels by the same
44 element as in the octahedral framework is observed for the first time in hollandite materials
45 and may be important in the understanding of their physical properties. It should be noticed
46 that A-cation vacancies were recently reported in nanorods of silver hollandite $\text{Ag}_x\text{Mn}_8\text{O}_y$ ²⁰,
47 but no Mn was detected inside empty channels. In this regard, an important question arises
48 about the real atomic arrangements in the wide channels and how they are related to the
49 structure of the nominal $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$.
50
51
52
53
54
55
56
57

58 The structural model which allows the simulation of different situations within the wide
59 channels was constructed starting with the reported crystal structure data of $\text{Bi}_{1.625}\text{V}_8\text{O}_{16}$ ²⁵⁻²⁶
60 as follows. The symmetry of the structure was chosen to $P4_1$ with the unit cell parameters

1
2
3 from the model are $a = a_{\text{Bi}_{1.625}\text{V}_8\text{O}_{16}}$ and $c = 4c_{\text{Bi}_{1.625}\text{V}_8\text{O}_{16}}$. At the first stage, the positions of
4 the vanadium and oxygen atoms from the single crystal structure determination were used
5 without changes. The bismuth atoms were located along the wide channel axis at $00z$ and
6 $\frac{1}{2}\frac{1}{2}z$ with the primary shift by $0.1045c_{\text{Bi}_{1.625}\text{V}_8\text{O}_{16}}$ and $0.6045c_{\text{Bi}_{1.625}\text{V}_8\text{O}_{16}}$ taking into account
7 the position of Bi atoms found in the X-ray diffraction experiment²⁵⁻²⁶. This model 1 with the
8 ideal composition $\text{Bi}_2\text{V}_8\text{O}_{16}$ describes well the HAADF-STEM contrast in many regions of
9 the experimental image (Fig. 4a). The case of the complete absence of bismuth atoms in one
10 of the channel at the $\frac{1}{2}\frac{1}{2}z$ is described with model 2 (lattice parameters as in model 1). Here,
11 the $00z$ axis is occupied by Bi atoms as in model 1 (Fig. 4b), and the additional V ions are
12 located at the channel of Bi-missing atoms, leading to the limit hypothetical $\text{Bi}_1\text{V}_1\text{V}_8\text{O}_{16}$. The
13 additional vanadium atoms are located around the $\frac{1}{2}\frac{1}{2}z$ axis replacing the missing Bi, close to
14 the wall of the channel employing the available oxygen atoms to form tetrahedral
15 environment and yielding the composition $\text{Bi}_1\text{V}_1\text{V}_8\text{O}_{16}$. In order to keep V-O distances in
16 reasonable limits, the oxygen atoms were slightly shifted from their ideal positions in the
17 crystal structure of $\text{Bi}_{1.7}\text{V}_8\text{O}_{16}$. A maximum intensity search was used to find the positions of
18 atomic columns of additional vanadium and adjacent oxygens. The calculated and
19 experimental HAADF-STEM contrasts for model 2 are shown in Figure 4b.

20
21 For modelling the mixed occupation of the $\frac{1}{2}\frac{1}{2}z$ axis (models 3 and 4), the unit cell
22 have to be doubled in the $[001]$ direction: $a = a_{\text{Bi}_{1.7}\text{V}_6\text{O}_{18}}$ and $c = 8c_{\text{Bi}_{1.7}\text{V}_6\text{O}_{18}}$ (Figure 4c). The
23 V/Bi ratio on the $\frac{1}{2}\frac{1}{2}z$ axis is 3/1 (model 3) or 2/2 (model 4). In order to keep large enough
24 distance of Bi to the vanadium in this channel, the bismuth atoms were shifted from the axis
25 toward the wall. Both models 3 (composition $\text{Bi}_{1.25}\text{V}_{0.75}\text{V}_8\text{O}_{16}$) and 4 (composition
26 $\text{Bi}_{1.5}\text{V}_{0.5}\text{V}_8\text{O}_{16}$) describe well fine details of contrast in the experimental HAADF-STEM
27 images (Figures 4c and 4d).

28
29 In order to confirm the stability of the proposed defect structure, we carried out first-
30 principles calculations within the framework of the density functional theory. The defect
31 structure was modeled as a rectangular $2 \times 2 \times 4$ supercell where a column of Bi atoms was
32 replaced with V (Fig. 5). The supercell with such defect configuration contained 28 Bi, 256 O
33 and 132 V atoms (in total 416 atoms). Such defect configuration was found to be stable, as
34 also confirmed by repeating the calculations with initial random displacement of all the atoms
35 within 0.1 \AA . The zoomed panel in Figure 5 on the right-hand side shows the details of the
36 atomic structure in the defect area. It is evident that atoms $\text{V}_1 - \text{V}_4$ are located at different
37 'heights', which breaks the symmetry and gives rise to the changes in the positions of
38 neighboring Bi atoms as observed in Fig. 3d. This effect may be in part due to spurious
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 interaction between the images of the defects, as the supercell used was rather small. We also
4 found a metastable configuration where atoms $V_1 - V_4$ were displaced by about 0.3 Å away
5 from the center of the channel, but this configuration was higher in energy by 1.3 eV. The
6 TEM images simulated using the DFT-optimized geometry for the input, proved to be in a
7 good agreement with the experimental data.
8

9
10
11 The final composition in case of such Bi-by-V substitution is $V_2V_8O_{16}$, i.e. $V_{10}O_{16}$, this would
12 yield the average valence of $\nu_V = 3.2$ and whereby the tetrahedral coordination of the
13 additional position put into mind a possible presence of pentavalent vanadium.
14
15
16
17

18 19 20 21 Electronic state of vanadium

22 To probe the change of the V oxidation state with Bi content x , electron energy loss
23 spectroscopy (EELS) was performed on three $Bi_xV_8O_{16}$ samples with nominal $x = 1.6, 1.7$ and
24 1.8 (Fig. 6). The fine structure of both the V- $L_{2,3}$ edge (520 eV and 513 eV) and the O- K edge
25 (532 eV) is known to be valence- and coordination-sensitive in vanadates. Three reference
26 vanadium oxides, V_2O_3 , V_2O_4 and V_2O_5 , were therefore also measured to allow a direct
27 comparison between our materials and the references. Judging by the onset and shape of the
28 V- $L_{2,3}$ edge, the vanadium in all three samples ($x = 1.6, 1.7$ and 1.8) appears to have a very
29 similar electronic state, being mainly a mixed V^{3+}/V^{4+} one, whereby the presence of small
30 amounts of V^{5+} is recognizable in particular at $x = 1.6$.
31
32
33
34
35
36
37
38
39

40 41 Physical properties

42 The impact of this simultaneous filling of channels on magnetic and transport
43 properties has been investigated in the case of $Bi_xV_8O_{16}$, with the nominal x values of 1.6 and
44 1.8. Magnetic susceptibility measured in a field of 100Oe is presented in Figure 7 for the two
45 x values. These measurements are consistent with the ones previously reported in ⁷, with very
46 low values of χ in the whole field range ($\approx 10^{-2}$ emu/mol), a high T maximum of χ close to
47 200 – 250 K typical of low dimensional magnets, and a low-T upturn at 60 K. For $x = 1.6$, χ
48 is characteristic of a Pauli paramagnet. In the case of $x = 1.8$, the low-T upturn at 60 K is very
49 sharp. NMR experiments have shown that it can be attributed to the presence of $V^{3+} - V^{3+}$
50 pairs, coexisting with V^{4+} paramagnetic spins ⁸. The temperature of 60 K corresponds as well
51 to the metal-to-insulator transition as observed in the inset of Figure 7 for $x = 1.8$, with a
52 strong increase of ρ observed below 60 K, when entering in the spin singlet phase ⁸⁻⁹. On the
53
54
55
56
57
58
59
60

1
2
3 other hand, the $x = 1.6$ sample exhibits only a moderate increase of ρ by two orders of
4 magnitude down to 2 K, in contrast with the 8 orders of magnitude observed for $x = 1.8$. The
5 values of resistivity and the large differences observed between $x = 1.6$ and $x = 1.8$ are in
6 good agreement with the ones previously published⁷. Above 200 K, both materials exhibit
7 very small values of ρ of few $\text{m}\Omega\cdot\text{cm}$, almost constant up to 950 K.

8
9
10
11
12 The thermopower of $\text{Bi}_x\text{V}_8\text{O}_{16}$ is presented in Figure 8. The values are negative in the
13 whole temperature range (5 – 950 K) for the two x concentrations. The magnitude of S
14 continuously increases up to 1000 K, to $\sim 35\text{-}40\mu\text{V}\cdot\text{K}^{-1}$. In the two curves, S presents a
15 minimum in magnitude at approx. 150 K, followed by a rapid increase of $|S|$ below 150 K. In
16 the most insulating compound ($x = 1.8$), S can be measured only down to 40 K, and the
17 transition at 60 K is observed, with a more rapid increase of $|S|$ below 60 K, as shown by the
18 dashed line in Figure 8. On the other hand, in the case of the more metallic $\text{Bi}_{1.6}\text{V}_8\text{O}_{16}$, S can
19 be measured down to 5 K. A clear transition is observed at 60 K, and S tends to zero, with a
20 linear behavior characteristic of a metal below 15K.

21
22 Above 200 K, these two curves are similar to the one of $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$ previously reported
23¹⁰, with S close to $-40\mu\text{V}\cdot\text{K}^{-1}$ at 900 K, and a sharp increase of $|S|$ below 140 K. This sharp
24 increase had been attributed to the occurrence of charge and orbital ordering, also observed on
25 the resistivity curve. The electrical and magnetic transition observed at 60 K for $x = 1.8$ has
26 the same impact on S , with an increase of the slope $d|S|/dT$ below 60 K. The minimum of
27 $\chi(T)$ at 60 K corresponds to the low-T transition in $S(T)$ (shown by the dashed line in figure
28 8). For $x = 1.8$, the transition towards a more resistive behavior observed at 60 K has thus a
29 direct impact on S , as expected, but the thermopower measurements suggest a possible second
30 transition at 150 K, which would be very similar to the one at 140 K in $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$. The
31 possible origin of this transition is not clear and will deserve further investigation. It must
32 also be stressed that, even if ρ increases at low T for $x = 1.6$, the increase is not as steep as for
33 $x = 1.8$ and the $S(T)$ curve is characteristic of a metallic transport down to low T , suggesting a
34 different low T ground state for $x = 1.6$. The magnetic transition at 60K is also smoother than
35 for $x = 1.8$,

36
37
38 These Seebeck experiments raise several questions. First of all, in a simple picture of
39 V^{4+} carriers doped in a V^{3+} matrix, thermopower should be positive. This is not the case, as
40 previously shown in $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$. According to the Heikes equation $S = \frac{-k_B}{e} \ln\left(\frac{1-x}{x}\right)$ as
41 more carriers are introduced³⁴, the magnitude of S should decrease, but the magnitude of S

1
2
3 actually does not change significantly. The thermopower needs thus to be described in a more
4 complex manner. The high-T Seebeck tends to $-35 \mu\text{V}\cdot\text{K}^{-1}$ and, as previously discussed¹⁰,
5 this is very close to the spin entropy term associated to a mixed valence of $\text{V}^{3+} (3d^2) / \text{V}^{4+}$
6 ($3d^1$). Considering a generalized Keikes formula³⁵, a spin and orbital entropy term has to be
7 added to the calculation of S with $S = \frac{-k_B}{e} \ln\left(\frac{1-x}{x}\right) - \frac{k_B}{e} \ln\left(\frac{g_3}{g_4}\right)$, where $g_3 = \Gamma_{\text{orb}}(\text{V}^{3+})$
8
9
10
11
12
13
14 $\Gamma_{\text{spin}}(\text{V}^{3+})$ and $g_4 = \Gamma_{\text{orb}}(\text{V}^{4+}) \Gamma_{\text{spin}}(\text{V}^{4+})$ reflect the orbital and spin degeneracy terms for V^{3+}
15 and V^{4+} , respectively. In these hollandites, S seems to be dominated by the spin entropy term,
16 which is equal to $\frac{-k_B}{e} \ln\left(\frac{2S_{\text{V}^{3+}} + 1}{2S_{\text{V}^{4+}} + 1}\right) = \frac{-k_B}{e} \ln\left(\frac{3}{2}\right) = -35 \mu\text{V}\cdot\text{K}^{-1}$, $S_{\text{V}^{3+}}$ and $S_{\text{V}^{4+}}$ being the
17 spins of V^{3+} and V^{4+} . This predominance of spin entropy has already been observed in
18 ruthenates such as SrRuO_3 ³⁶ or Sr_2RuO_4 , and has been related to the freezing of orbital
19 fluctuations up to 950 K³⁷, revealing the dominant role of spin entropy on the thermopower in
20 this temperature range. It would be interesting to determine if such a freezing of orbital
21 fluctuations could also be at play in these vanadium hollandites.
22
23
24
25
26
27
28
29

30 The presence of two transitions in S(T) at ≈ 60 K and 150 K is puzzling. The one at 60 K
31 can be related to the minimum of magnetic susceptibility, but the one at 150 K does not
32 correspond to any other transition reported so far, and looks very similar to the one of
33 $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$, and almost at the same temperature. Due to the low-dimensional nature of the
34 hollandites, the magnetic fluctuations could play a crucial role on transport in a broad range of
35 temperature as discussed above, and the thermopower is often a very sensitive probe of these
36 fluctuations. Further work is needed to better understand the low-temperature transitions.
37
38
39
40
41
42

43 To conclude, resistivity measurements show metal-to-insulator transitions at low T (T =
44 60 K) observed both for $x = 1.6$ and $x = 1.8$, the transitions being much sharper for $x = 1.8$,
45 while the thermopower measurements suggest a more metallic ground state for $x = 1.6$ at low
46 T. The magnetic transition at 60K is also much sharper for $x = 1.8$. On the other hand, the
47 thermopower and resistivity are not very sensitive to x at high T, and the thermopower seems
48 to be dominated by the spin entropy associated to $\text{V}^{3+} / \text{V}^{4+}$ in this T range.
49
50
51
52
53
54

55 New features of the $\text{Bi}_x\text{V}_8\text{O}_{16}$ hollandite

56 The present study points towards different new features for the $\text{Bi}_x\text{V}_8\text{O}_{16}$ hollandite. For
57 $T > 200$ K, the electrical resistivity is x- and T-independent with values remaining all close to
58 few $\text{m}\Omega\cdot\text{cm}$. This semi-metallic behavior is accompanied with a negative Seebeck coefficient
59
60

1
 2
 3 which absolute $|S|$ value increases with T . At the highest measured T (950 K) S values are
 4 very close for $x = 1.6$ and $x = 1.8$ with $S \approx -35\mu\text{V}\cdot\text{K}^{-1}$. This suggests that S is dominated by
 5 the spin entropy term related to V^{3+} and V^{4+} when orbitals fluctuations are frozen and that the
 6 V formal valency calculated from the nominal $\text{Bi}_{1.6}\text{V}_8^{3.4+}\text{O}_{16}$ and $\text{Bi}_{1.8}\text{V}_8^{3.32+}\text{O}_{16}$ compositions
 7 is very close. These behaviors at high T contrast with the very different magnitude of the
 8 metal-to-insulator transition at $T \approx 60$ K when one compares the $x = 1.6$ and $x = 1.8$ samples.
 9 The χ - and ρ -coupled changes at T_{MI} are much more pronounced in $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$ than in
 10 $\text{Bi}_{1.6}\text{V}_8\text{O}_{16}$, and thermopower measurements reveal a metallic ground state at low T for $x =$
 11 1.6. However, from EELS it is not possible to detect a significant change in the effective
 12 valence ν_{V} as x increases from 1.6 to 1.8. The transition at 60 K is believed to be related to the
 13 fact that for $x = 1.8$, ν_{V} should be very close to 3.33, which is consistent with the existence of
 14 a 1:2 ratio for charge and orbital ordering invoked to explain the MIT as proposed in Ref. 7-9
 15 and evidenced by NMR showing a coexistence of spin-singlet $\text{V}^{3+}-\text{V}^{3+}$ with V^{4+} having a
 16 localized spin moment. Even though a $\text{V}^{3.33+}$ oxidation favors a concomitant charge and
 17 orbital ordering in the $(\text{VO}_6)_2$ stripes, lifting the triangular degeneracy, due to the electronic
 18 repulsion between the cations in the tunnel and extra charges of the neighboring stripes, it is
 19 expected that the A cations and vacancies tend to order. Thus, the possibility to get ordered or
 20 disordered chains of Bi^{3+} and vacancies in the large square tunnels is an important issue.
 21
 22
 23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35
 36
 37
 38
 39
 40
 41
 42
 43
 44
 45
 46
 47
 48
 49
 50
 51
 52
 53
 54
 55
 56
 57
 58
 59
 60

In that respect, the TEM study gives a different scenario about the filling up in the
 channels of the hollandite structure. Combining HAADF-STEM and image simulations data
 based on local structural models and supported by DFT calculations, it is demonstrated that
 the wider channels of the structure are mostly partially occupied by Bi^{3+} cations and this
 partial occupation is locally accompanied by extra vanadium cations shifted from the center of
 these channels. This compensation mechanism by replacement toward a virtual limit
 composition ' $\text{M}_2\text{M}_8\text{O}_{16}$ ' could also be at play in hollandites of other M metals. With such a
 mechanism, the formal metal oxidation state of the hollandite $\text{Bi}_{2-y}\text{V}_y\text{V}_8\text{O}_{16}$ could be kept
 constant: considering the actual compositions $\text{Bi}_{1.6}\text{V}_{8.4}\text{O}_{16}$ and $\text{Bi}_{1.8}\text{V}_{8.2}\text{O}_{16}$ for the $x = 1.6$ and
 $x = 1.8$ samples of our study, one obtains $\nu_{\text{V}} = 3.23$ and $\nu_{\text{V}} = 3.24$, respectively. As the V
 species in the tunnels are in tetrahedral coordination, one could also consider pentavalent
 vanadium in tetrahedral coordination which yields different ν_{V} for the vanadium cation in the
 $(\text{VO}_6)_2$ stripes, $(\text{Bi}_{1.6}\text{V}_{0.4}^{5+})\text{V}_8^{3.15+}\text{O}_{16}$ and $(\text{Bi}_{1.8}\text{V}_{0.2}^{5+})\text{V}_8^{3.20+}\text{O}_{16}$. Note that the corresponding
 cation ratio differ from the nominal ones. Nevertheless, this shift is very limited, with a Bi/V
 ratio equal to 0.220 and 0.225 for ' $\text{Bi}_{1.8}\text{V}_8$ ' and ' $\text{Bi}_{1.8}\text{V}_{8.2}$ ' respectively. Also, the presence of

1
2
3 vacancies in the tunnels cannot be completely ruled out. Though our observations do not
4 allow the exact quantification of Bi, V and vacancies in the tunnels, they point towards
5 differences in the electronic repulsion between these species and the extra charges on the V-O
6 network of the neighboring stripes. Especially, as the number of V species in the tunnel
7 increases as y increases according to an idealized $(\text{Bi}_{2-y}\text{V}_y)\text{V}_8\text{O}_{16}$ chemical formula, the
8 charge and orbital ordering in the V_8O_{16} framework should be hindered. This disorder effect
9 would explain the more pronounced transitions observed for the $x = 1.8$ sample than for the x
10 $= 1.6$ one, rather than a pure electronic scenario related to the ν_V shift from 3.3 as one goes
11 from $\text{Bi}_{1.8}\text{V}_8^{3.325+}\text{O}_{16}$ to $\text{Bi}_{1.6}\text{V}_8^{3.475+}\text{O}_{16}$.
12
13
14
15
16
17
18
19

20 21 **Conclusion**

22 The TEM study of the hollandite $\text{Bi}_x\text{V}_8\text{O}_{16}$ revealed the presence of additional V species
23 located together with Bi in the channels of the crystal structure. The vanadium fillers
24 occupying off-centered atomic positions in the channels have tetrahedral coordination (V^{5+})
25 differently from the octahedral one (V^{3+} , V^{4+}) in the V_8O_{16} framework. The average value of
26 the vanadium oxidation state calculated from the new model of this hollandite differs from
27 that obtained by considering the nominal composition $\text{Bi}_x\text{V}_8\text{O}_{16}$. As a consequence, rather x -
28 independent value of the Seebeck coefficient S could be attributed to the new vanadium
29 oxidation state which exhibits an x -independent value. In contrast, the disorder introduced
30 from channel to channel by the coexisting V and Bi could impact the setting of the charge and
31 orbital ordering, explaining why the transition is smeared out when the Bi nominal content x
32 decreases. The question now is to understand if this concomitant filling of the channels by
33 Bi^{3+} and vanadium is related to the Bi^{3+} lone pair and/or the versatility of vanadium to adopt
34 different coordination and oxidation states in oxides. Considering the potential applications of
35 these hollandites for nuclear waste storage, electrodes, or as photocatalysis, these results
36 highlight the importance of a local investigation of the channels to better understand the
37 relationship between the octahedra network and the channel fillers, and thus better understand
38 the doping mechanism and the disorder influence.
39
40
41
42
43
44
45
46
47
48
49
50
51
52

53 **Acknowledgments**

54
55
56
57 Yu.G. acknowledge the Caen University for the position of Visiting Professor. The authors
58 thanks N. Gauquelin for providing EELS data. A.V.K. thanks the Academy of Finland for
59 financial support through Projects no. 286279 and the Ministry of Education and Science of
60

1
2
3 the Russian Federation in the framework of Increase Competitiveness Program of NUST
4 “MISiS” (#K2-2015-033), and the CSC-IT Center for Science Ltd for generous grants of
5 computer time.
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

References

1. Isobe, M.; Koishi, S.; Yamazaki, S.; Yamaura, J.; Gotou, H.; Yagi, T.; Ueda, Y., Substitution Effect on Metal–Insulator Transition of $K_2V_8O_{16}$, *J. Phys. Soc. Jpn.* **2009**, *78*, 114713.
2. Isobe, M.; Koishi, S.; Kouno, N.; Yamaura, J.; Yamauchi, T.; Ueda, H.; Gotou, H.; Yagi, T.; Ueda, Y., Observation of Metal–Insulator Transition in Hollandite Vanadate, $K_2V_8O_{16}$, *J. Phys. Soc. Jpn.* **2006**, *75*, 073801.
3. Toriyama T., Nakao A., Yamaki Y., Nakao H., Murakami Y., Hasegawa K., Isobe M., Ueda Y., Ushakov A. V., Khomskii D. I., Streltsov S. V., Konishi T., Ohta Y., Peierls Mechanism of the Metal-Insulator Transition in Ferromagnetic Hollandite $K_2Cr_8O_{16}$, *Phys. Rev. Lett.* **2011**, *107*, 266402.
4. Kuwabara, T.; Isobe, M.; Gotou, H.; Yagi, T.; Nishio-Hamame, D.; Ueda, Y., Synthesis, Structure, and Electromagnetic Properties of Manganese Hollandite, $K_xMn_8O_{16}$, *J. Phys. Soc. Jpn.* **2012**, *81*, 104701.
5. Ozawa, T.; Suzuki, I.; Sato, H., Structural, Magnetic and Electronic Transport Properties of Novel Hollandite-Type Molybdenum Oxide, $Rb_{1.5}Mo_8O_{16}$, *J. Phys. Soc. Jpn.* **2006**, *75*, 014802.
6. Sato, H.; Enoki, T.; Yamaura, J.; Yamamoto, N., Charge localization and successive magnetic phase transitions of mixed-valence manganese oxides $K_{1.5}(H_3O)_xMn_8O_{16}$ $0 < x < 0.5$, *Phys. Rev. B* **1999**, *59*, 12836- 12841.
7. Kato, H.; Waki, T.; Kato, M.; Yoshimura, K.; Kosuge, K., Temperature-Induced Metal-Insulator Transition in $Bi_xV_8O_{16}$, *J. Phys. Soc. Jpn.* **2001**, *70*, 325- 328.
8. Waki, T.; Kato, H.; Kato, M.; Yoshimura, K., Metal–Insulator Transition in $Bi_xV_8O_{16}$: ^{51}V NMR Study, *J. Phys. Soc. Jpn.* **2004**, *73*, 275 – 279.

- 1
2
3 9. Waki, T.; Kato, M.; Yoshimura, K., Observation of spin-singlet state in $\text{Bi}_x\text{V}_8\text{O}_{16}$,
4
5 *Physica B* **2005**, 359 – 361, 1309- 1311.
- 6
7
8 10. Maignan, A.; Lebedev, O.I.; Van Tendeloo, G.; Martin, C.; Hébert, S., Metal to
9
10 insulator transition in the *n*-type hollandite vanadate $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$, *Phys. Rev. B* **2010**, 82,
11
12 035122.
- 13
14
15 11. Ishiwata S., Bos J. W. G., Huang Q., Cava, R. J., Structure and magnetic properties of
16
17 hollandite $\text{Ba}_{1.2}\text{Mn}_8\text{O}_{16}$, *J. Phys.: Condens. Matter* **2006**, 18, 3745–3752.
- 18
19
20 12. Crespo, Y.; Andreev, A.; Seriani, N., Competing antiferromagnetic and spin-glass
21
22 phases in a hollandite structure, *Phys. Rev. B* **2013**, 88, 014202.
- 23
24
25 13. Larson A. M. , Moetakef P., Gaskell K., Brown C. M., King G. and Rodriguez E. E.,
26
27 Inducing Ferrimagnetism in Insulating Hollandite $\text{Ba}_{1.2}\text{Mn}_8\text{O}_{16}$, *Chem. Mater.* **2015**, 27,
28
29 515 -525.
- 30
31
32 14. Sooran Kim S., Kim B. H., Kim K., Min B. I., Metal-insulator transition in a spin-
33
34 orbital-lattice coupled Mott system: $\text{K}_2\text{V}_8\text{O}_{16}$, *Phys. Rev. B* **2016**, 93, 045106.
- 35
36
37 15. Huang, J.; Poiraz, A.S.; Takeuchi, K.J.; Takeuchi, E.S.; Marschilok, A.C. $\text{M}_x\text{Mn}_8\text{O}_{16}$ (M
38
39 = Ag or K) as promising cathode materials for secondary Mg based batteries: the role of
40
41 the cation M, *Chem. Comm* **2016**, 52, 4088- 4091.
- 42
43
44 16. Mori T., Yamauchi S., Yamamura H., Watanabe M. , New hollandite catalysts for the
45
46 selective reduction of nitrogen monoxide with propene, *Applied Catalysis A* 1995, 129,
47
48 L1 – L7.
- 49
50
51 17. Krishna, SR, Shrujana, P, Palla, S, Sreenu, K, Velchuri, R, Vithal, M. , Preparation,
52
53 characterization and photocatalytic studies of $\text{K}_2\text{Al}_2\text{Ti}_6\text{O}_{16}$, $\text{K}_{2-x}\text{Ag}_x\text{Al}_2\text{Ti}_6\text{O}_{16}$ and
54
55 $\text{K}_2\text{Al}_2\text{Ti}_6\text{O}_{16-x}\text{N}_y$, *Materials Research Express* **2015**, 2, 035008.
- 56
57
58 18. Bursill, L.A.; Smith, J., Electron irradiation effects in (Cs, Ba) – hollandites, *J.Solid*
59
60 *State Chem.* **1987**, 69, 343- 354.

- 1
2
3 19. Tumurugoti P., Clark B. M., Edwards D. J., Amoroso J., Sundaram S. K., Cesium
4 incorporation in hollandite-rich multiphasic ceramic waste forms, *J. Solid Stat. Chem.*
5 **2017**, 246, 107 -112.
6
7
8
9
10 20. Wu, L.; Xu, F.; Zhu, Y.; Brady, A.B.; Huang, J.; Durham, J.L.; Dooryhee, E.;
11 Marschilok, A.C.; Takeuchi, E.S.; Takeuchi, K.J., Structural Defects of Silver
12 Hollandite, $\text{Ag}_x\text{Mn}_8\text{O}_y$, Nanorods: Dramatic Impact on Electrochemistry, *ACS Nano*
13 **2015**, 9, 8430- 8439.
14
15
16
17
18
19 21. Laurita G., Grajczyk R., Stolt M., Coutinho I., Sleight A. W., Subramanian M. A.,
20 Influence of Structural Disorder on Hollandites $\text{A}_x\text{Ru}_4\text{O}_8$ ($\text{A}^+ = \text{K}, \text{Rb}, \text{Rb}_{1-x}\text{Na}_x$), *Inorg.*
21 *Chem.* **2016**, 55, 3462–3467.
22
23
24
25
26
27 22. Carter, M.L., Withers, R.L., An electron and X-ray diffraction study of the compositely
28 modulated barium nickel hollandite $\text{Ba}_x(\text{Ni}_x\text{Ti}_{8-x})\text{O}_{16}$, $1.16 < x < 1.32$, solid solution,
29 *Z.Kristallogr.* **2004**, 219, 763- 767.
30
31
32
33
34 23. Carter, M.L., Withers, R.L., A universally applicable composite modulated structure
35 approach to ordered $\text{Ba}_x\text{M}_y\text{Ti}_{8-y}\text{O}_{16}$ hollandite-type solid solutions, *J. of Solid State*
36 *Chem* **2005**, 178, 1903 - 1914.
37
38
39
40
41 24. Nistor, L.C., Van Tendeloo, G., Amelinckx, S., Defects and phase transitions in natural
42 monoclinic hollandite: $\text{Ba}_x\text{Mn}_8\text{O}_{16}$, *J. of Solid State Chem* **1994**, 109, 152- 165.
43
44
45
46 25. Mentré, O., Abraham, F. New Mixed Valence Compounds in the Pb–V–O System:
47 Synthesis and Crystal Structure of Hollandite-Related $\text{Pb}_{1.32}\text{V}_{8.35}\text{O}_{16.7}$ and R-Type
48 Hexagonal Ferrite $\text{PbV}_6\text{O}_{11}$, *J. of Solid State Chem* **1996**, 125, 91 - 101.
49
50
51
52
53 26. Abraham, F.; Mentré, O. $\text{Bi}_{1.7}\text{V}_8\text{O}_{16}$ – The first Bi- hollandite type compound, *J. of*
54 *Solid State Chem* **1994**, 109, 127- 133.
55
56
57
58 27. Momma, K.; Izumi, F., VESTA 3 for three-dimensional visualization of crystal,
59 volumetric and morphology data, *J. Appl. Crystallogr* **2011**, 44, 1272- 1276.
60

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
28. Koch, C.T. **2002** Determination of core structure periodicity and point defect along dislocations *PhD thesis* Arizona State University.
 29. Kresse, G.; Hafner, J. Ab- initio molecular dynamics for liquid metals, *Phys. Rev. B* **1993**, *47*, 558- 561.
 30. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **1996**, *54*, 11169- 11186.
 31. Perdew, J.P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple, *Phys. Rev. Lett* **1996**, *77*, 3865- 3868.
 32. Blöchl, P.E., Projector augmented- wave method, *Phys. Rev B.* **1994**, *50*, 17953- 17979.
 33. Hytch, M.J.; Snoeck, E.; Kilaas, R. Quantitative measurement of displacement and strain fields from HREM micrographs, *Ultramicroscopy* **1998**, *74*, 131- 146.
 34. Chaikin, P.M.; Beni, G., Thermopower in the correlated hopping regime, *Phys. Rev. B* **1976**, *13*, 647- 651.
 35. Koshibae, W.; Tsutsui, K.; Maekawa, S., Thermopower in cobalt oxides, *Phys. Rev. B* **2000**, *62*, 6869- 6872.
 36. Klein, Y.; Hébert, S.; Maignan, A.; Kolesnik, S.; Maxwell, T.; Dabrowski, B., Insensitivity of the band structure of substituted SrRuO₃ as probed by Seebeck coefficient measurements, *Phys. Rev. B* **2006**, *73*, 052412.
 37. Mravjle, J.; Georges, A., Thermopower and Entropy: Lessons from Sr₂RuO₄, *Phys. Rev. Lett.* **2016**, *117*, 036401.

Figure Legends

Fig 1: a) Powder XRD pattern of $\text{Bi}_{1.6}\text{V}_8\text{O}_{16}$ (space group $I4/m$) with the indexation of the first Bragg peaks. Insert: b) VO_6 octahedra (blue) highlighting the narrow and wide tunnels containing Bi cations (red) in a perspective view along the [001] direction and c) the triangular ladder-like vanadium sublattice (yellow) with the shortest V-V distances (in Å) in a view along [100]

Fig. 2: ED patterns and HRTEM image of $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$: (a) ED patterns along the main zone axes [001], [100] and [111]. Notice appearance of diffuse linear reflections in the [100] and [111] ED patterns marked by white arrows; (b) [001] HRTEM image and an enlargement with overlapped structural model as insert.

Fig. 3: HRTEM on $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$:
(a) [001] High resolution HAADF-STEM image with an enlargement and structural overlay model in insert (Bi – brown, V-yellow, O-blue).
(b) [100] High resolution HAADF-STEM image and corresponding FT pattern, notice diffuse scattering around 0hl spots similar to that of ED in Fig 2a.
(c) Enlargement of selected area in (b) and corresponding intensity plot profile along Bi row (marked with white arrows) indicating presence of differently occupied Bi columns. The columns with the Bi deficiency depicted with white arrowhead in the figure and black arrow in the intensity plot profile.
(d) Enlargement image of [100] HAADF-STEM overlaid with structural model (Bi – brown, V-yellow, O-blue). Notice splitting Bi atoms due to A-cation split position with partial occupancy reported for $\text{Bi}_{1.625}\text{V}_8\text{O}_{16}$ ²⁵⁻²⁶. Red arrows head pointed out the absence one of the two Bi atoms in some columns.

Fig. 4: Experimental (cf. Figure 4a) and simulated HAADF-STEM images of $\text{Bi}_{1.8}\text{V}_8\text{O}_{16}$ based on structural models of different atomic arrangements in the wide channels: (a) model 1 (no bismuth defects on the 00z and $\frac{1}{2}1/2z$ axes, composition $\text{Bi}_2\text{V}_8\text{O}_{16}$) in projection along [001] and [100] directions; (b) model

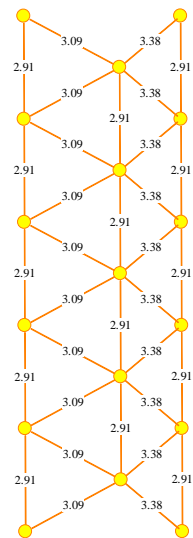
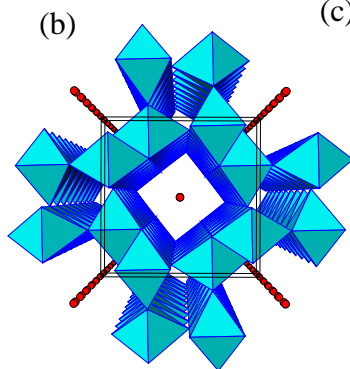
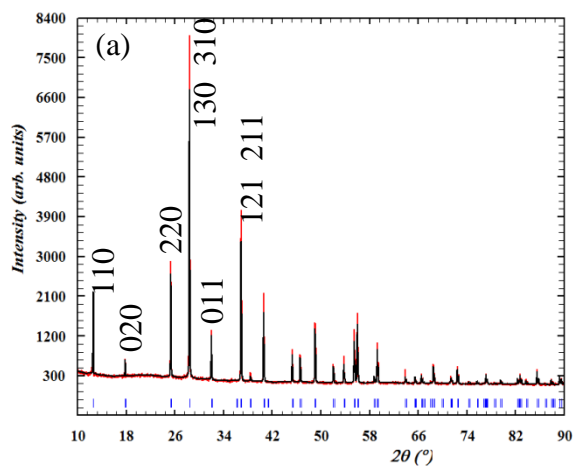
1
2
3 2 (complete bismuth absence on the channel axis $\frac{1}{2}\frac{1}{2}z$, replaced by the
4 vanadium atoms located at the wall of the tunnel, composition $\text{Bi}_1\text{V}_1\text{V}_8\text{O}_{16}$) in
5 projection along [001] and [100] directions; (c) model 3 (mixed occupation of
6 the channel axis $\frac{1}{2}\frac{1}{2}z$ with V/Bi ratio 3/1, composition $\text{Bi}_{1.25}\text{V}_{0.75}\text{V}_8\text{O}_{16}$) in
7 projection along [001] and [100] directions; (d) model 4 (mixed occupation of
8 the channel axis $\frac{1}{2}\frac{1}{2}z$ with V/Ba ratio 1/1, composition $\text{Bi}_{1.5}\text{V}_{0.5}\text{V}_8\text{O}_{16}$) in
9 projection along [001] and [100] directions.
10
11
12
13
14
15
16

17 Fig. 5: The line defect structure of $\text{Bi}_{1.75}\text{V}_{0.25}\text{V}_8\text{O}_{16}$ in the ball-and-stick representation as
18 revealed by density functional theory calculations. A column of Bi atoms (brown
19 balls) was replaced by V atoms (yellow). Blue dashed line shows the periodic
20 supercell used in the calculations (top orthographic view). The panel on the right-
21 hand side shows the details of the atomic structure in the defect area (perspective
22 view).
23
24
25
26
27
28

29 Fig. 6: Energy loss near edge spectra of V- $L_{2,3}$ edge and O- K edge of three V oxide
30 references together with the investigated samples $\text{Bi}_x\text{V}_6\text{O}_{18}$ ($x=1.8$, $x=1.7$, $x=1.6$).
31 The onset of the V- $L_{2,3}$ edge and the shape of both the V- $L_{2,3}$ and O- K fine
32 structures indicate the electronic state of V in $\text{Bi}_x\text{V}_6\text{O}_{18}$ being mainly a mixture of
33 V^{3+} and V^{4+} with small contributions of V^{5+} .
34
35
36
37
38
39

40 Fig. 7: Magnetic susceptibility $\chi(T)$ measured in a field of 100 Oe for $x = 1.6$ (squares)
41 and $x = 1.8$ (triangles). Inset: Electrical resistivity of $\text{Bi}_x\text{V}_8\text{O}_{16}$ measured up to 950
42 K for $x = 1.6$ (squares) and $x = 1.8$ (triangles).
43
44
45
46

47 Fig. 8: Seebeck coefficient of $\text{Bi}_x\text{V}_8\text{O}_{16}$ measured up to 950 K for $x = 1.6$ (squares) and x
48 $= 1.8$ (triangles). These values are compared to the ones of $\text{Pb}_{1.6}\text{V}_8\text{O}_{16}$ previously
49 reported [9] (stars). The dashed line corresponds to $T = 60$ K, i. e. the metal-to-
50 insulator transition temperature.
51
52
53
54
55
56
57
58
59
60



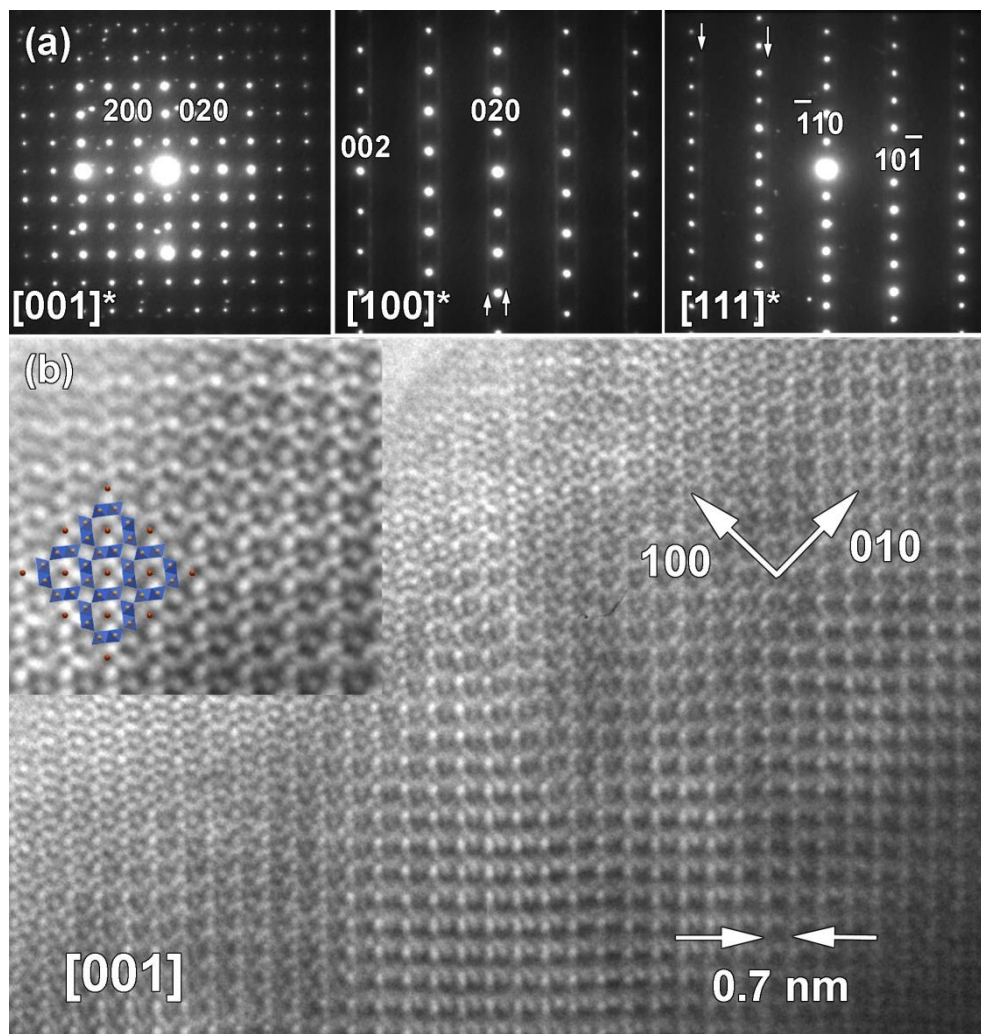


Figure 2

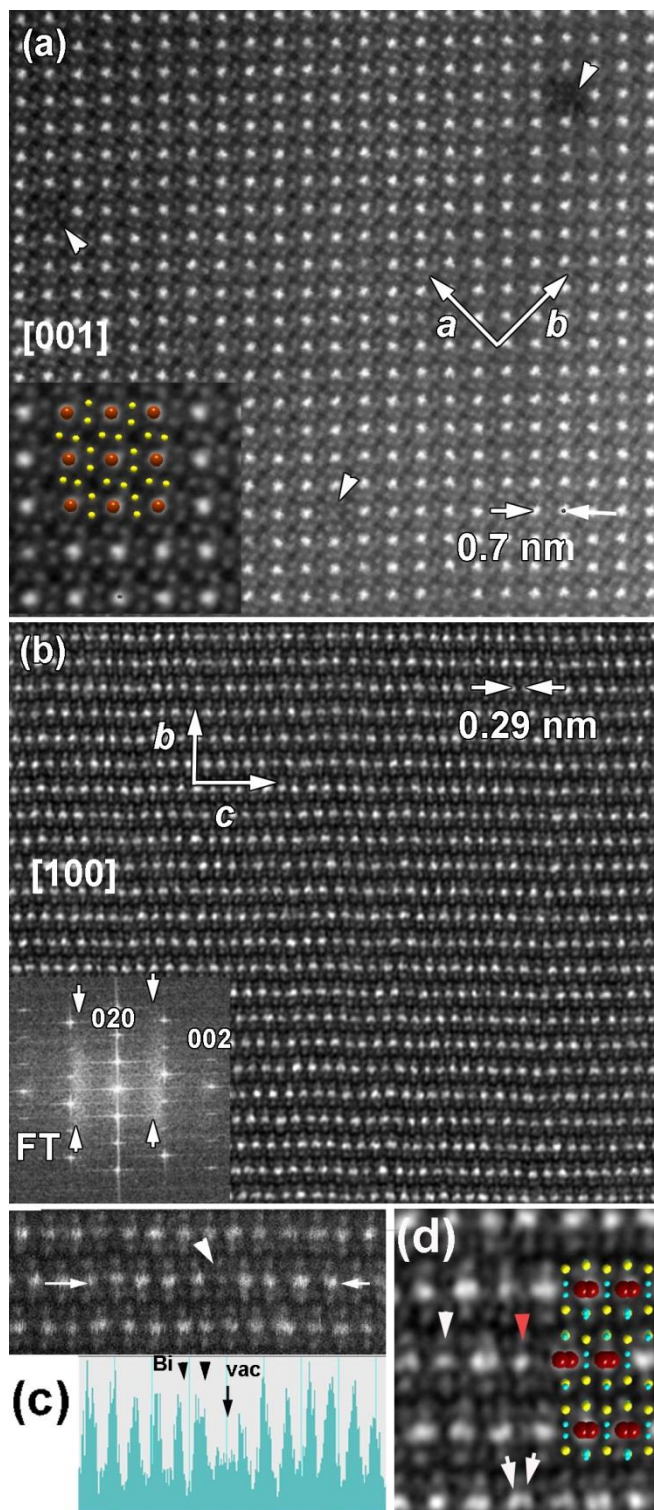


Figure 3

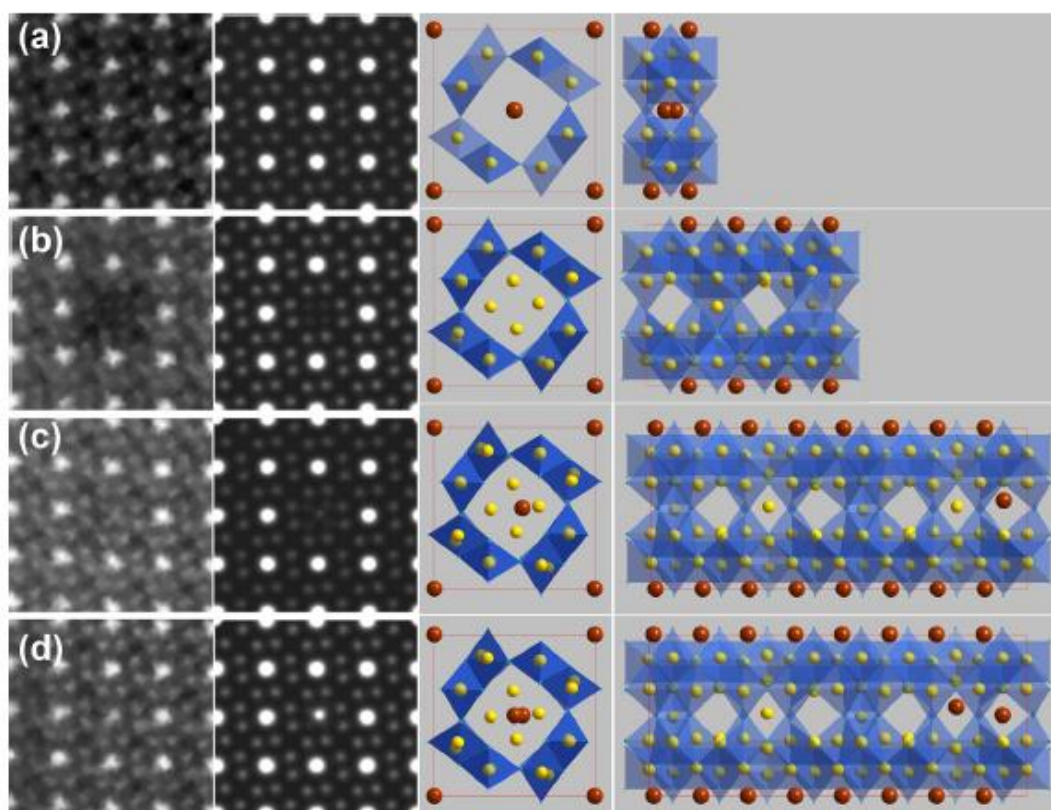


Figure 4

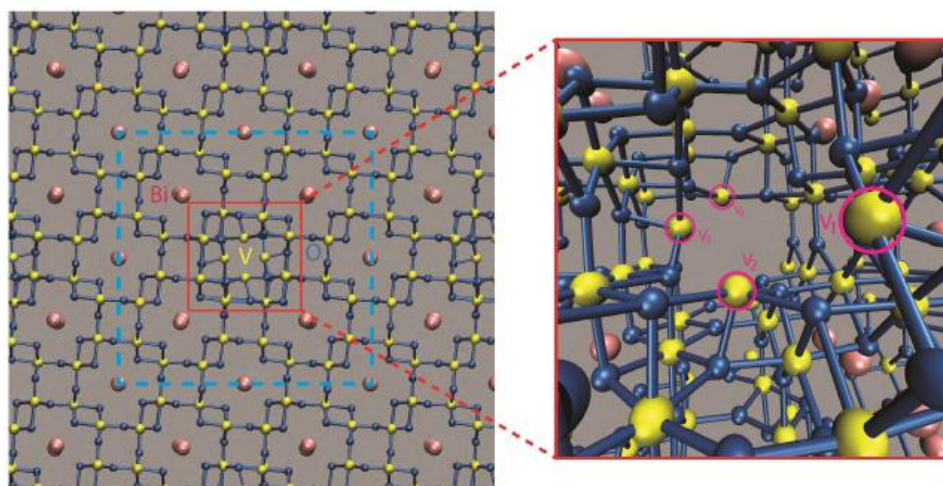


Figure 5

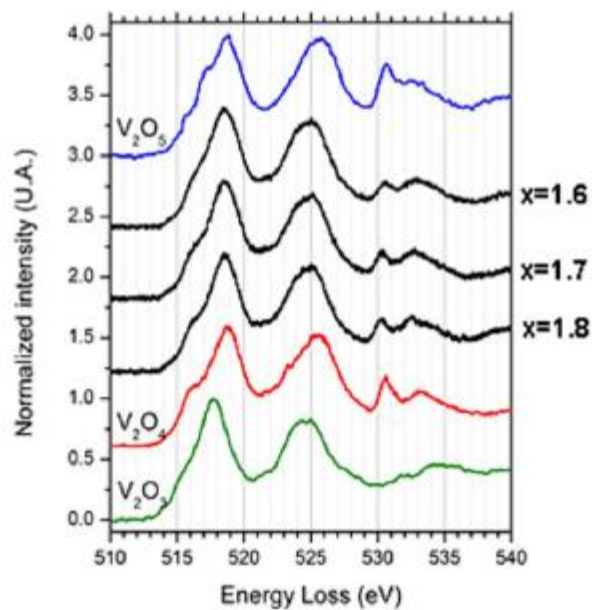


Figure 6

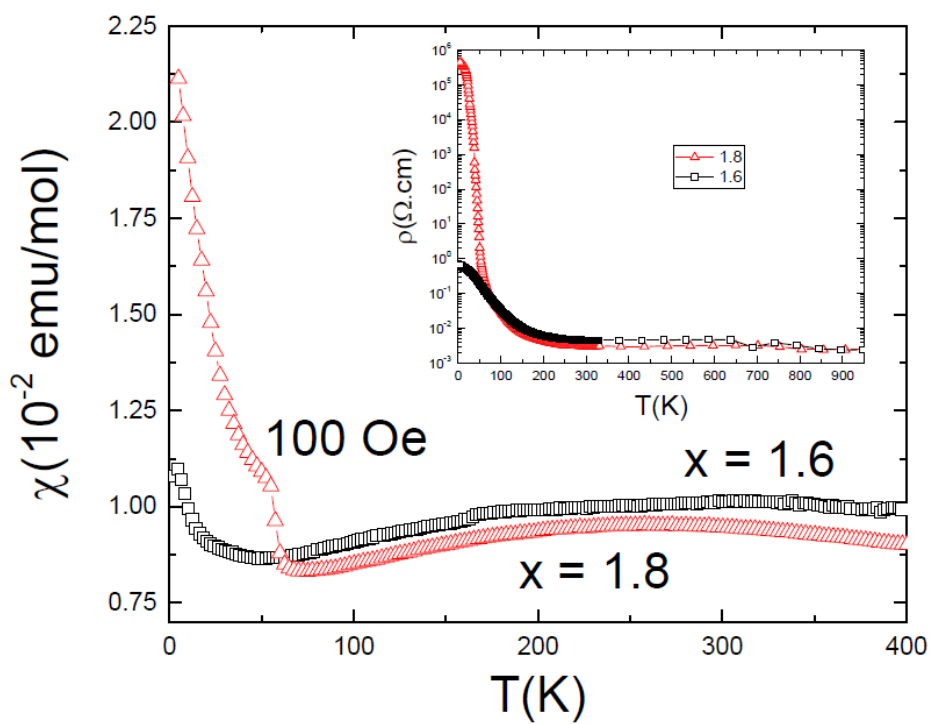


Figure 7

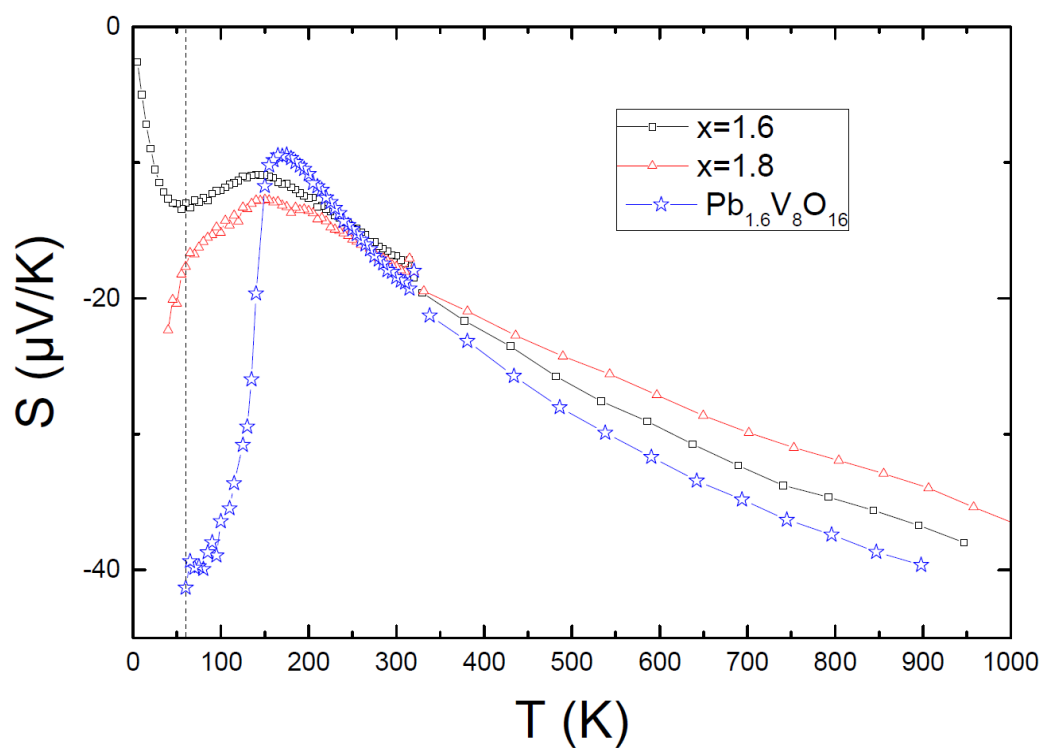


Figure 8