### **Supporting Information**

### Unconventional Stable Stoichiometry of Vanadium Peroxide

Xin Du<sup>‡</sup>, Jing Zhang<sup>‡</sup>, Hong Yu, Jianyan Lin, Shoutao Zhang, and Guochun Yang<sup>\*</sup>

Centre for Advanced Optoelectronic Functional Materials Research and Key Laboratory for UV Light-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China

\*Address correspondence to: yanggc468@nenu.edu.cn

Index Page
1. Computational details ······2
<b>2.</b> Calculated Birch-Murnaghan equation of states for $P$ -1-structured VO <sub>4</sub> ······4
<b>3.</b> Phonon dispersion curves for predicted stable V-O compounds
4. Electronic band structures of predicted stable V-O compounds ( $Fmm2-V_2O$ ,
<i>P</i> 6 <sub>3</sub> / <i>mmc</i> -VO, <i>P</i> -1-VO <sub>4</sub> )······6
<b>5.</b> Electron localized function of VO <sub>4</sub> at 140 GPa······7
<b>6.</b> Bader charge of V in $VO_4$ as a function of pressure $\cdots 7$
7. Projected electronic densities of states of VO <sub>4</sub> ······8
<b>8.</b> The PDOS of $P$ -1 VO <sub>4</sub> at different pressures
<b>9.</b> Spin-dependent PDOS of VO <sub>4</sub> with <i>P</i> -1symmetry10
<b>10.</b> Phonon dispersion curve and superconductive property of $V_2O$ at 0 GPa $\cdots$ 10
11. The lattice parameters for V-O compounds compared with previous works at
ambient pressure 11
<b>12.</b> Structural information of predicted stable V-O compounds
13. The calculated lowest unoccupied molecular orbital (LUMO) values of peroxide
group (O <sub>2</sub> <sup>2-</sup> )·····13
<b>14.</b> References

#### **Computational Details**

Our structural prediction approach is based on a global minimization of free energy surfaces merging ab initio total-energy calculations with CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in the CALYPSO code.<sup>1,2</sup> The structures of stoichiometry  $V_m O_n$  (m = 1, n = 1-5; m = 2, n = 1, 3, and 5) were searched with simulation cell sizes of 1 - 4 formula units (f.u.) at the selected pressures of 1 atm and 50, 100, 200 GPa. In the first step, random structures with certain symmetry are constructed in which atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using the VASP code<sup>3</sup> were done with the conjugate gradients method and stopped when total energy changes became smaller than  $1 \times 10^{-5}$  eV per cell. After processing the first generation structures, 60% of them with lower enthalpies are selected to construct the next generation structures by PSO (Particle Swarm Optimization). 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency. In most cases, structural searching simulations for each calculation were stopped after generating  $1000 \sim 1200$  structures (e.g., about  $20 \sim 30$  generations).

To further analyze the structures with higher accuracy, we select a number of structures with lower enthalpies and perform structural optimization using density functional theory within the generalized gradient approximation<sup>4</sup> as implemented in the VASP code. The cut-off energy for the expansion of wavefunctions into plane waves is set to 750 eV in all calculations, and the Monkhorst–Pack *k*-mesh with a maximum spacing of 0.03 Å<sup>-1</sup> was individually adjusted in reciprocal space with respect to the size of each computational cell. This usually gives total energy well converged within ~1 meV/atom. The electron-ion interaction was described by means of projector augmented wave with  $3s^23p^63d^44s^1$  and  $2s^22p^4$  electrons as valence for V and O atoms, respectively.

In order to further test the reliability of the adopted pseudopotentials for V and O, the validity of the projector augmented wave (PAW) pseudopotentials from the VASP library is checked by comparing the calculated Birch-Murnaghan equation of state with that obtained from the full-potential linearized augmented plane-wave method (LAPW) using local orbitals (as implemented in WIEN2k).<sup>5</sup> The Birch-Murnaghan equation of states derived from PAW and LAPW methods are almost identical (Figure. S0). Thus, our adopted pseudopotentials are feasible in the range of 0~200 GPa.

The phonon spectra and electron-phonon coupling calculations are carried out with the density functional perturbation (linear response) theory as implemented in the QUANTUM ESPRESSO package.<sup>6</sup> We employ the ultrasoft pseudopotentials with  $3d^34s^2$ , and  $2s^22p^4$  as valence electrons for V, and O atoms, respectively. The kinetic energy cutoff for wave-function expansion is chosen as 120 Ry. To reliably calculate electron-phonon coupling in metallic systems, we need to sample dense k-meshes for electronic Brillouin zone integration and enough q-meshes for evaluating average contributions from the phonon modes. Dependent on specific structures of stable compounds, the k-meshes and q-meshes are used:  $16 \times 16 \times 16$  k-meshes and  $4 \times 4 \times$ 4 q-meshes for V<sub>2</sub>O in the *Fmm*2 structure. We have calculated the superconducting  $T_c$  of metallic V<sub>2</sub>O as estimated from the McMillan-Allen-Dynes formula<sup>7-9</sup>

$$T_{C} = \frac{\omega_{\log}}{1.2k_{B}} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^{*}(1+0.62\lambda)}\right]$$

Here,  $k_{\rm B}$  is the Boltzmann constant and  $\mu^*$  is the Coulomb pseudopotential ( $\mu^* = 0.1$ ). The electron-phonon coupling constant,  $\lambda$ , and the logarithmic average phonon frequency,  $\omega_{\rm log}$ , are calculated by the Eliashberg spectral function for electron-phonon interaction:  $\alpha^2 F(\omega) = \frac{1}{N(E_{\kappa})} \sum_{kav} |g_{k,k+q,v}|^2 \delta(\varepsilon_k) \delta(\varepsilon_{k+q}) \delta(\omega - \omega_{q,v})$ 

where  $\lambda = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega}$ ;  $\omega_{\log} = \exp\left[\frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega)\right]$ . Herein,  $N(E_F)$  is the electronic density of states at the Fermi level,  $\omega_{q,v}$  is the phonon frequency of mode v and wave vector q, and  $|g_{k,k+q,v}|$  is the electron-phonon matrix element between two electronic states with momenta k and k + q at the Fermi level<sup>10,11</sup>

# **Supporting Figures**



**Figure S0.** Comparison of the fitted Birch-Murnaghan equation of states for  $VO_4$  with *P*-1 symmetry by using the calculated results from the PAW pseudopotentials and the full-potential LAPW methods.



**Figure S1.** Phonon dispersion curves for predicted V–O compounds. (a)  $Fmm2-V_2O$  at 80 GPa. (b)  $P6_3/mmc$ -VO at 120 GPa. (c) P-1-VO<sub>4</sub> at 140GPa.



**Figure S2.** Electronic energy bands for stable V-O compounds. (a)  $Fmm2-V_2O$  at 80 GPa. (b)  $P6_3/mmc$ -VO at 120 GPa. (c)  $P-1-VO_4$  at 140 GPa.



**Figure S3.** Electron localized function of  $VO_4$  at 140 GPa. Here, the V-O bonds, contributed by four types of O in  $VO_4$ , are shown in (a), (b), (c), and (d), respectively. It clearly indicates that V-O bonds in  $VO_4$  are ionic.



Figure S4. Bader charge of V in VO<sub>4</sub> as a function of pressure.



**Figure S5.** Projected electronic densities of states of VO<sub>4</sub>. O1 is an atom from oxide ion (O<sup>2-</sup>) and O2, O3, and O4 are atoms from peroxide ions (O<sub>2</sub><sup>2-</sup>).



Figure S6. The PDOS of P-1 VO<sub>4</sub> at (a) 140, (b) 160, (c) 180, and (d) 200 GPa, respectively.



Figure S7. Spin-dependent PDOS of  $VO_4$  with *P*-1 symmetry at (a) 0 and (b) 140 GPa.



**Figure S8.** (a) Phonon dispersion curve of *Fmm*2 V<sub>2</sub>O at 0 GPa. (b) The Eliashberg spectral function  $\alpha^2 F(\omega)$  and integrated electron-phonon coupling parameters  $\lambda(\omega)$  of *Fmm*2 V<sub>2</sub>O at 0 GPa.

# **Supporting Tables**

Phases	Lattice Parameters (Å, °)	Lattice Parameters (Å, °)	
	(in our work)	(in other works)	
<i>Fm-3m-</i> VO <sup>12</sup>	<i>a</i> = 4.473 <i>a</i> = 4.062~4.12		
	<i>b</i> = 4.473	<i>b</i> = 4.062~4.125	
	<i>c</i> = 4.473	<i>c</i> = 4.062~4.125	
$R-3c-V_2O_3^{13}$	<i>a</i> = 5.157	<i>a</i> = 4.952	
	<i>b</i> = 5.157	<i>b</i> = 4.952	
	<i>c</i> = 14.106	<i>c</i> = 14.002	
<i>P</i> 2 <sub>1</sub> / <i>c</i> -VO <sub>2</sub> <sup>14</sup>	<i>a</i> = 5.443	<i>a</i> = 5.752	
	<i>b</i> = 4.514	<i>b</i> =4.538	
	<i>c</i> = 5.444	<i>c</i> = 5.383	
		(at 25 °C)	
$Pmmn-V_2O_5^{15}$	<i>a</i> = 11.534	<i>a</i> = 11.512	
	<i>b</i> = 3.635	<i>b</i> =3.564	
	c = 4.715	c = 4.368	

**Table S1.** The lattice parameters for V-O compounds compared with previous works at ambient pressure (0 K).

Here, the large difference for VO originates from the measured experimental conditions. Its lattice parameters is measured at high temperature ( $800^{\circ}$ C) and oxygen vacancy (VO<sub>0.25</sub>-VO<sub>1.5</sub>).

Phases	Pressur	Lattice		Wyckoff	Positions	
	e	Parameters	(fractional)			
	(GPa)	(Å, °)	Atoms	x	У	z
Fmm2-V <sub>2</sub> O	80	a = 2.66700	V(8c)	0.50000	0.64365	0.99828
		b = 9.40980	O(4a)	0.00000	0.00000	0.64874
		c = 4.15510				
		$\alpha = 90.0000$				
		$\beta = 90.0000$				
		$\gamma = 90.0000$				
P6 <sub>3</sub> /mmc-VO	120	<i>a</i> = 2.44260	V(2a)	0.00000	0.00000	0.00000
		<i>b</i> = 2.44260	O(2c)	0.66670	0.33330	0.75000
		c = 5.42630				
		$\alpha = 90.0000$				
		$\beta = 90.0000$				
		$\gamma = 120.000$				
<i>P</i> -1-VO <sub>4</sub>	140	<i>a</i> =3.28310	V(2i)	0.69036	0.71468	0.72715
		<i>b</i> =4.37830	O(2i)	0.73200	0.47529	0.35723
		c = 4.47200	O(2i)	0.63616	0.15253	0.94534
		$\alpha = 97.8123$	O(2i)	0.19609	0.01699	0.52538
		$\beta = 99.8834$	O(2i)	0.89826	0.30904	0.90728
		$\gamma = 70.3473$				

 Table S2. Crystallographic data of predicted stable V-O compounds.

**Table S3.** The calculated lowest unoccupied molecular orbital (LUMO) values of peroxide group  $(O_2^{2-})$  with different O-O distances at MP2/6-311G(*d*,*p*) level of theory, which come from the VO<sub>4</sub> at 140 and 200 GPa, respectively.

	VO <sub>4</sub> at 140 GPa	VO <sub>4</sub> at 200 GPa
O-O Distance/Å	1.32	1.29
LUMO/eV	14.4	15.29

#### References

- 1 Y. Wang, J. Lv, L. Zhu and Y. Ma, Crystal structure prediction via particleswarm optimization, *Phys. Rev. B*, 2010, **82**, 94116.
- 2 Y. Wang, J. Lv, L. Zhu and Y. Ma, CALYPSO: A method for crystal structure prediction, *Comput. Phys. Commun.*, 2012, **183**, 2063–2070.
- G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio totalenergy calculations using a plane-wave basis set, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, *Phys. Rev. B*, 1992, 46, 6671–6687.
- 5 P. Blaha, K. Schwarz, P. Sorantin and S. B. Trickey, Full-potential, linearized augmented plane wave programs for crystalline systems, *Comput. Phys. Commun.*, 1990, **59**, 399–415.
- P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni and I. Dabo, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *J. Phys. Condens. matter*, 2009, 21, 395502.
- L. N. Oliveira, E. K. U. Gross and W. Kohn, Density-Functional Theory for Superconductors, *Phys. Rev. Lett.*, 1988, 60, 2430–2433.
- M. Lüders, M. A. L. Marques, N. N. Lathiotakis, A. Floris, G. Profeta, L. Fast,
   A. Continenza, S. Massidda and E. K. U. Gross, Ab initio theory of superconductivity. I. Density functional formalism and approximate functionals, *PhysRevB.*, 2005, 72, 024545.
- M. A. L. Marques, M. Lueders, N. N. Lathiotakis, G. Profeta, A. Floris, L. Fast,
   A. Continenza, E. K. U. Gross and S. Massidda, Ab initio theory of superconductivity. II. Application to elemental metals, *Phys. Rev. B*, 2005, 72, p.024546.1-024546.13.

- 10 P. B. Allen and B. Mitrovic, Theory of Superconducting  $T_c$ , Solid State Phys., 1982, **37**, 1–92.
- J. P. Carbotte, Properties of boson-exchange superconductors, *Rev. Mod. Phys.*, 1990, **62**, 1027.
- 12 C. WESTMAN, SVEN and NORDMARK, within the VOU-25\\_V01. 5 Region at 800 C, *Acta Chem. Scand.*, 1960, **14**, 465–470.
- 13 Y. Newnham, RE and de Haan, Refinement of the a A1<sub>2</sub>O, Ti<sub>2</sub>O, V<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O, structures, *Zeits. Krist*, 1962, **117**, 235–237.
- P. and others Longo, John M and Kierkegaard, A refinement of the structure of VO<sub>2</sub>, *Acta Chem. Scand*, 1970, 24, 420–426.
- R. Enjalbert and J. Galy, A refinement of the structure of V<sub>2</sub>O<sub>5</sub>, *Acta Crystallogr. Sect. C*, 1986, 42, 1467–1469.