

## *Wadsley vanadium oxides*

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*Wadsley* vanadium oxides form a homologous series  $V_nO_{2n+1}$  between the end members  $\alpha$ - $V_2O_5$  and  $VO_2(B)$ . They exhibit a variety of crystal structures due to different polyhedra around the  $V^{4+}$  and  $V^{5+}$  cations and polyhedral connectivity. Their structural features as well as transport and magnetic properties are reviewed here. The *Wadsley* vanadium oxides are oxygen deficient with different ordered vacancies in the oxygen cubic close-packing array. The rutile-type structure, with the oxygen hexagonal close packing, is found in  $V_6O_{13}$  ( $n = 6$ ) obtained at high pressures and high temperatures, which unlike its  $\alpha$  polymorph stable at atmospheric conditions, does not undergo a metal-insulator phase transition. This finding opens a possibility of synthesizing new materials with unexpected properties in the system  $V_2O_5$ -  $VO_2$  by varying compositions and exerting extreme conditions.

**Table S1** Summary of the space group symmetries, synthesis methods, V-V distances, and properties for the rutile-type and VO<sub>2</sub>(S) vanadium dioxides.

Compound	Space group	Synthesis method	V-V distances	Properties	Ref.
VO <sub>2</sub> (R)	<i>P4<sub>2</sub>/mnm</i> ( <i>Z</i> = 2) a = 4.5546(1) Å c = 2.8528(1) Å V = 59.2 Å <sup>3</sup>	Phase transition from M1 above 341 K	Equal V-V distances, linear chain	Metallic	14-17, 19
VO <sub>2</sub> (M1)	<i>P2<sub>1</sub>/c</i> ( <i>Z</i> = 4) a = 5.752(3) Å b = 4.538(3) Å c = 5.383(3) Å β = 122.65(10)° V = 115.6 Å <sup>3</sup>	Atomic layer deposition, pulsed laser deposition, chemical vapor deposition, solgel, solid state reactions, hydrothermal methods	Strong V-V dimerization, alternating V-V distances	Insulator	5, 14-18
VO <sub>2</sub> (M2)	<i>C2/m</i> ( <i>Z</i> = 8) a = 9.0664(7) Å b = 5.7970(5) Å c = 5.37725(6) Å β = 115.3372(7)° V = 237.5 Å <sup>3</sup>	Phase transition from M1  Solid state reaction V <sub>2</sub> O <sub>3</sub> /V <sub>2</sub> O <sub>5</sub>	Partial V-V dimerization, one paired chain + one zigzag chain	Insulator	14-17, 19, 20
VO <sub>2</sub> (T)	<i>P1</i> ( <i>Z</i> = 4) a = 9.06 Å b = 5.7721(1) Å c = 4.5203(1) Å α = 89.99(1)° β = 91.40(1)° γ = 89.93(1)° V = 236.32 Å <sup>3</sup>	Phase transitions from M1 and M2	Moderate V-V dimerization, three inequivalent V-V distances	Insulator	14-17, 20
VO <sub>2</sub> (M1')	<i>P2<sub>1</sub>/c</i> ( <i>Z</i> = 4)	Isostructural phase transition from M1 at 13.9 GPa	Weak V-V dimerization, reduced bond alternation compared to M1	Insulator	26
VO <sub>2</sub> (O)	<i>Pnmm</i> ( <i>Z</i> = 4)	Phase transition from R at 13.7 GPa and 383 K	Nearly uniform V-V distances, very weak bond alternation	Insulator	28
VO <sub>2</sub> (X)		Phase transitions from M1' at 34.3 as well as from O at 38.3 GPa and 383 K	Dimer collapse, nearly uniform V-V distances	Metallic	27-31
VO <sub>2</sub> (S)	<i>P3</i> ( <i>Z</i> = 7) a = 7.35632(3) Å c = 4.52364(3) Å V = 212.00 Å <sup>3</sup>	Solid state reaction V <sub>2</sub> O <sub>3</sub> /V <sub>2</sub> O <sub>5</sub> at high pressures	Nearly uniform V-V distances, residual distortion present	Insulator	32
V <sub>0.995</sub> O <sub>2</sub>	<i>P2/m</i> ( <i>Z</i> = 2) a = 4.506 Å b = 2.899 Å c = 4.617 Å b = 91.79° V = 60.3 Å <sup>3</sup>	Solid state reaction V <sub>2</sub> O <sub>3</sub> /V <sub>2</sub> O <sub>5</sub> at high pressures	Reduced dimerization, reduction in long range dimer coherence	Metallic above 353 K and 361 K, respectively	33
V <sub>0.976</sub> O <sub>2</sub>	<i>P2/m</i> ( <i>Z</i> = 2)	Solid state reaction V <sub>2</sub> O <sub>3</sub> /V <sub>2</sub> O <sub>5</sub> at high pressures		Metallic above 361 K	33

**Table S2** Summary of the space group symmetries, synthesis methods, V-V distances, and properties for the Wadsley phases, including V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub>(B) and VO<sub>2</sub>(A).

Compound	Space group	Synthesis method	V-V distances	Properties	Ref.
$\alpha$ -V <sub>2</sub> O <sub>5</sub>	<i>Pmmn</i> ( <i>Z</i> = 2) a = 11.5165(4) Å b = 3.5585(1) Å c = 4.324(1) Å V = 177.2 Å <sup>3</sup>	Chemical/physical vapor deposition  Crystallization from a solution  Crystallization from a melt	V-V distances > 3.4 Å	Semiconductor	35, 37, 40
$\beta$ -V <sub>2</sub> O <sub>5</sub>	<i>P2<sub>1</sub>/m</i> ( <i>Z</i> = 2) a = 7.1140(2) Å b = 3.57178(1) Å c = 6.28460(2) Å $\beta$ = 90.069(3)° V = 159.7 Å <sup>3</sup>	High-pressure synthesis	V-V distances >3.2 Å	Semiconductor	38-40
$\delta$ -V <sub>2</sub> O <sub>5</sub>	<i>C2/c</i> ( <i>Z</i> = 4) a = 11.9719(2) Å b = 4.7017(1) Å c = 5.3253(1) Å $\beta$ = 104.41° V = 290.32 Å <sup>3</sup>	High-pressure synthesis	Intralayer V-V distances >3.3 Å, larger interlayer V-V distances	Semiconductor	39, 40
V <sub>3</sub> O <sub>7</sub>	<i>C2/c</i> ( <i>Z</i> = 12) a = 21.921(3) Å b = 3.679(1) Å c = 18.341(2) Å $\beta$ = 95.61(1)° V = 1472.07 Å <sup>3</sup>	Solid state reaction V <sub>2</sub> O <sub>5</sub> /V <sub>2</sub> O <sub>3</sub>	V-V distances in chains >3. Å, longer interchain distances >3.4 Å	Insulator, Uniaxial ferromagnet	58-60
V <sub>3.047</sub> O <sub>7</sub>	<i>P3</i> ( <i>Z</i> = 2) a = 7.35136(2) Å c = 4.51462(2) Å V = 211.29 Å <sup>3</sup>	Reduction of V <sub>2</sub> O <sub>5</sub> at high pressures	V-V distances unclear	Semiconductor	61
V <sub>4</sub> O <sub>9</sub>	<i>Pnma</i> ( <i>Z</i> = 4) a = 17.926(4) Å b = 3.631(1) Å c = 9.396(2) Å V = 611.58 Å <sup>3</sup>  <i>Cmcm</i> ( <i>Z</i> = 8) a = 10.356(2) Å b = 8.174(1) Å c = 16.559(3) Å V = 1401.7 Å <sup>3</sup>	Decomposition of V <sub>3</sub> O <sub>7</sub> in supercritical water at high pressures  Reduction of $\alpha$ -V <sub>2</sub> O <sub>5</sub>  Reduction of $\alpha$ -V <sub>2</sub> O <sub>5</sub>	Short V-V distances along chains (2.8-2.9 Å), longer interchain distances (>3.3 Å)  No V-V chains	  Antiferromagnet	56  57 62
$\alpha$ -V <sub>6</sub> O <sub>13</sub>	<i>C2/m</i> ( <i>Z</i> = 2) 150 K – RT a = 11.922(1) Å b = 3.680(1) Å c = 10.138(2) Å $\beta$ = 100.87(2)° V = 436.80 Å <sup>3</sup>  <i>Pc</i> ( <i>Z</i> = 2) below 150 K a = 10.0605(4) Å b = 3.7108(3) Å	Solid state reaction V <sub>2</sub> O <sub>5</sub> /V <sub>2</sub> O <sub>3</sub> , chemical vapor transport	Equidistant V-V zigzags both in the single and double layers  Alternating zigzag V-V distances in the	Metallic  Insulator, paramagnet down to 55 K, antiferromagnet below 55 K	63-66  70-74

