Electronic Supplemental Information

$ZnVO_3$: An ilmenite-type vanadium oxide hosting robust V–V dimers

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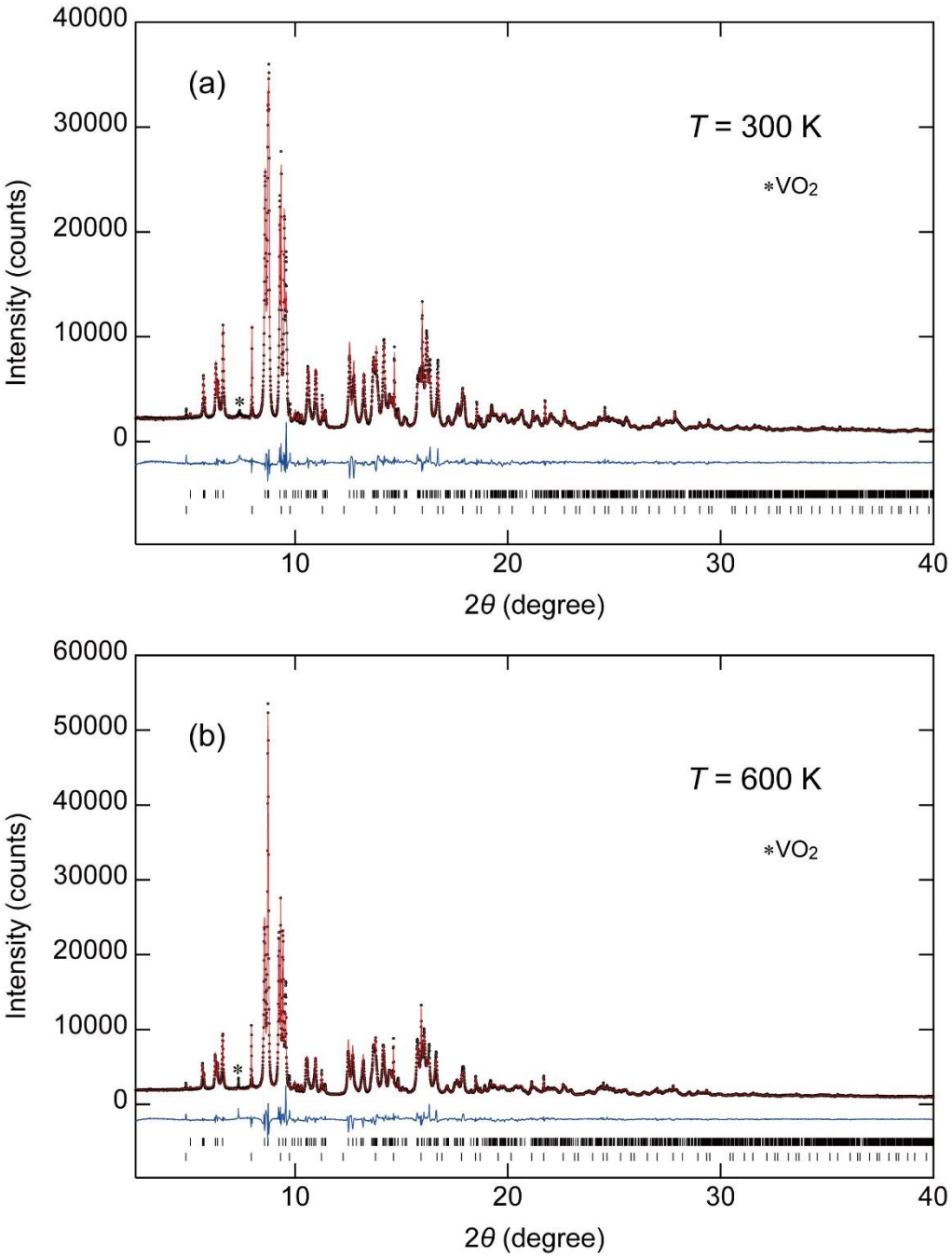

Fig. S1. (a) Rietveld refinement result for the $ZnVO_3$ sample at 300 K. (b) Rietveld refinement result for the $ZnVO_3$ sample at 600 K. The black points and red lines represent the observed and calculated SXRD patterns, respectively; the blue line denotes their difference. The tick markers indicate the positions of the Bragg reflections of the triclinic $ZnVO_3$ (upper) and spinel-type ZnV_2O_4 (lower) phases. The star marks indicate reflections from VO_2.

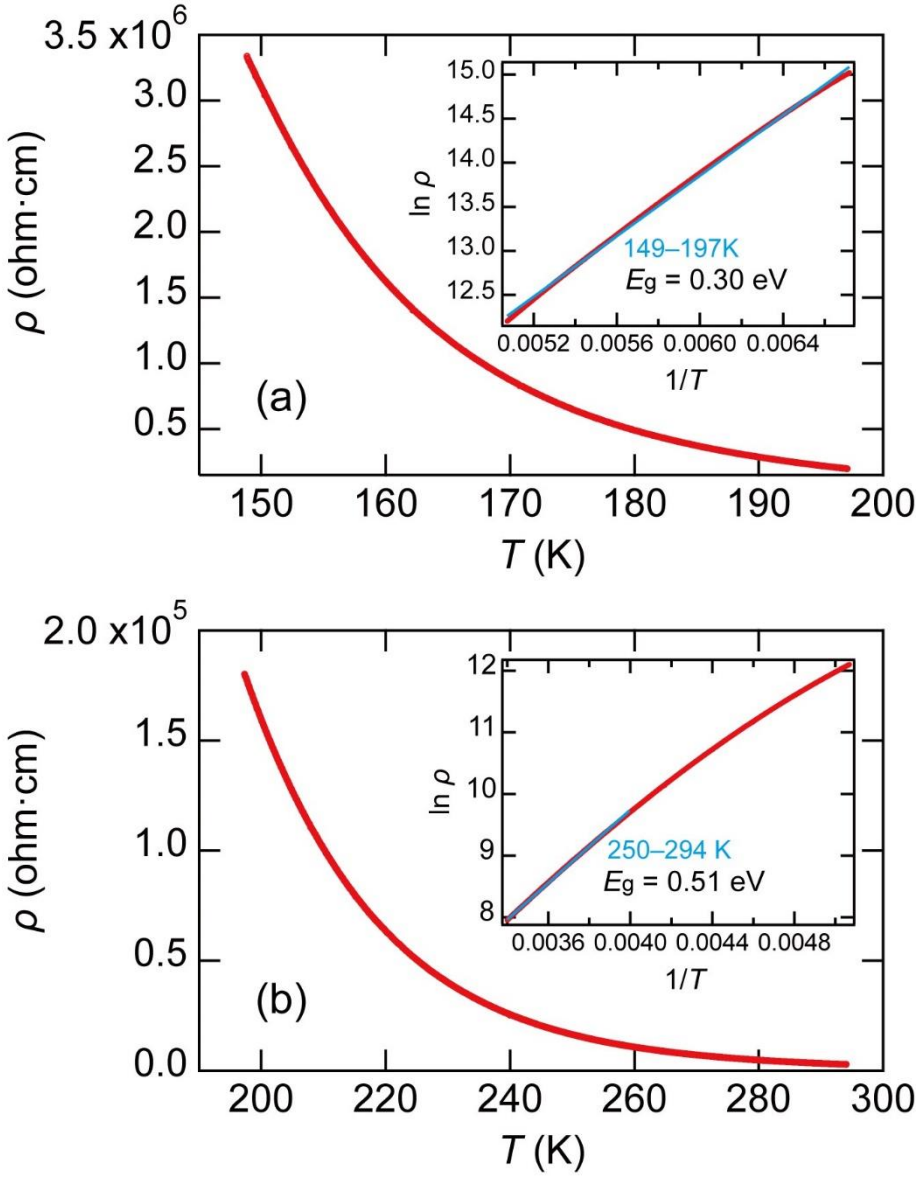

Fig. S2. (a) Electrical resistivity of the $ZnVO_3$ sample between 149–197 K. Inset shows the Arrhenius plot and the fitting result (light blue line). (b) Electrical resistivity of the $ZnVO_3$ sample between 198–294 K. Inset shows the Arrhenius plot and the fitting result between 250–294 K (light blue line).

Table S1. Refined structural parameters of $ZnVO_3$ at 300 K.

atom	site	occ.	*x*	*y*	*z*	*B* (Å^2)
Zn1	2i	1	0.6309(3)	0.6230(3)	0.6592(3)	0.27(2)
V1	2i	1	0.1711(4)	0.1401(4)	0.1412(4)	0.27(2)
O1	2i	1	0.7849(10)	0.4511(12)	0.0237(12)	0.16(6)
O2	2i	1	0.5766(11)	0.9330(13)	0.2324(11)	0.16(6)
O3	2i	1	0.9271(11)	0.1935(13)	0.5900(12)	0.16(6)

Space group: $P\bar{1}$ (No. 2), $Z = 2$, The temperature factors (B) of the Zn and V atoms were assumed to be equal. The temperature factors (B) of the O atoms were assumed to be equal.

Table S2. Lattice parameters and agreement factors of $ZnVO_3$ at 300 K.

parameter	obtained value
a (Å)	5.4534(6)
b (Å)	5.5658(7)
c (Å)	5.4889(6)
α (degree)	53.222(6)
β (degree)	55.666(6)
γ (degree)	53.976(6)
V (Å^3)	101.99(2)
ρ_{calc}	5.351 g/cm^3
R_{wp}	5.120%
R_B ($ZnVO_3$)	1.653%
R_B (ZnV_2O_4)	3.724%

Table S3. Refined structural parameters of $ZnVO_3$ at 600 K.

atom	site	occ.	*x*	*y*	*z*	*B* (Å^2)
Zn1	2i	1	0.6323(4)	0.6219(4)	0.6550(4)	0.60(3)
V1	2i	1	0.1628(5)	0.1440(5)	0.1464(5)	0.60(3)
O1	2i	1	0.7780(14)	0.4613(16)	0.0190(16)	1.00(7)
O2	2i	1	0.5905(16)	0.9201(17)	0.2245(14)	1.00(7)
O3	2i	1	0.9327(14)	0.1970(17)	0.5882(15)	1.00(7)

Space group: $P\bar{1}$ (No. 2), $Z = 2$, The temperature factors (B) of the Zn and V atoms were assumed to be equal. The temperature factors (B) of the O atoms were assumed to be equal.

Table S4. Lattice parameters and agreement factors of $ZnVO_3$ at 600 K.

parameter	obtained value
a (Å)	5.4708(8)
b (Å)	5.5818(8)
c (Å)	5.4856(8)
α (degree)	53.324(8)
β (degree)	55.894(7)
γ (degree)	54.221(8)
V (Å^3)	103.08(3)
ρ_{calc}	5.294 g/cm^3
R_{wp}	6.057%
R_B ($ZnVO_3$)	2.530%
R_B (ZnV_2O_4)	4.746%

Redefinition of the unit cell of ilmenite-type $MgVO_3$. In this study, we redefined the unit cell of ilmenite-type $MgVO_3$, departing from previous conventions. The unit cell was redefined based on the rhombohedral structure to ensure clarity and consistency in characterization. To prevent any confusion, we present the redefined lattice and structural parameters of $MgVO_3$ in Tables S3 and S4. The crystallographic data were extracted from reference 7.

Table S5. Refined structural parameters of $MgVO_3$ at 300 K (SXRD).

atom	site	occ.	*x*	*y*	*Z*	*B* (Å^2)
Mg1	2i	0.9822	0.6445	0.6394	0.6522	0.17
V1	2i	0.0178	0.6445	0.6394	0.6522	0.17
V2	2i	0.9867	0.1676	0.1395	0.1417	0.17
Mg2	2i	0.0133	0.1676	0.1395	0.1417	0.17
O1	2i	1	0.7736	0.4493	0.0403	0.39
O2	2i	1	0.0627	0.7822	0.4233	0.39
O3	2i	1	0.4348	0.0626	0.7643	0.39

[a]Space group: $P\bar{1}$ (No. 2), $Z = 2$.

Table S6. Lattice parameters of $MgVO_3$ at 300 K (SXRD).

parameter	obtained value
a (Å)	5.4137
b (Å)	5.4349
c (Å)	5.5399
α (degree)	53.541
β (degree)	54.753
γ (degree)	54.744
V (Å^3)	100.022