Supporting Information

Improved Oxide Ion Conductivity of Hexagonal Perovskite-Related Oxides $Ba_3W_{1+x}V_{1-x}O_{8.5+x/2}$

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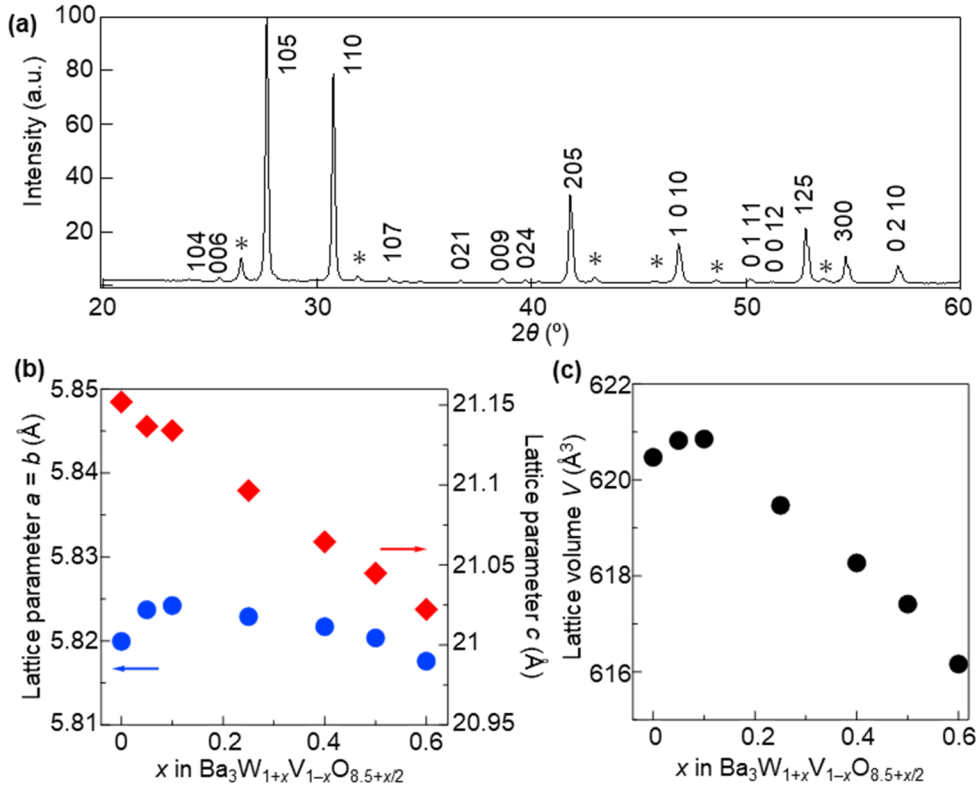

Figure S1. X-ray powder diffraction pattern of $Ba_3W_{1.6}V_{0.4}O_8$, lattice parameters and lattice volume of $Ba_3W_{1+x}V_{1-x}O_{8.5+x/2}$ as functions of excess W content *x*. (a) X-ray powder diffraction pattern of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ sample. *hkl* denotes the reflection index of the main rhombohedral phase based on the hexagonal setting. The asterisk symbol represents peak position from a small amount of impurity phase $BaWO_4$. (b) Lattice parameters and (c) lattice volume of $Ba_3W_{1+x}V_{1-x}O_{8.5+x/2}$ (x = 0, 0.05, 0.1, 0.25, 0.4, 0.5, 0.6 and 0.75) as a function of the excess W content x. The error bars in (b) and (c) are within the symbols.

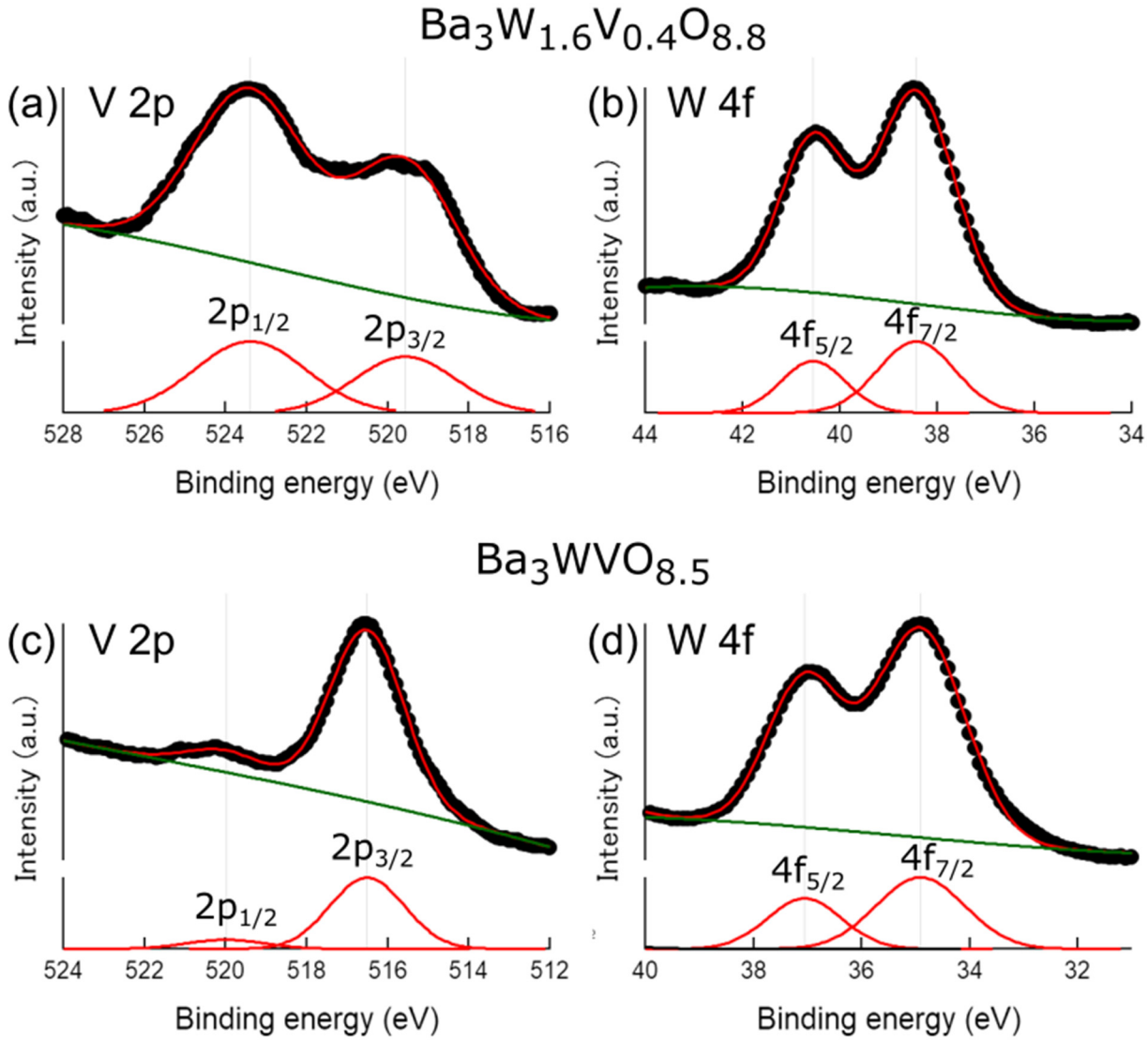

Figure S2. XPS spectra of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ and $Ba_3WVO_{8.5}$. (a) V 2p and (b) W 4f XPS spectra of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ and (c) V 2p and (d) W 4f spectra of $Ba_3WVO_{8.5}$. For each panel, black points, red solid lines, and green lines represent observed intensities, fitted curves, and background, respectively. The binding energies of W and V in the measured samples are, respectively, close to the values of W^{6+} in WO_3 and V^{5+} in V_2O_5 [1–3]. Therefore, the oxidation states of W and V in $Ba_3WVO_{8.5}$ and $Ba_3W_{1.6}V_{0.4}O_{8.8}$ are assigned to be W^{6+} and V^{5+}.

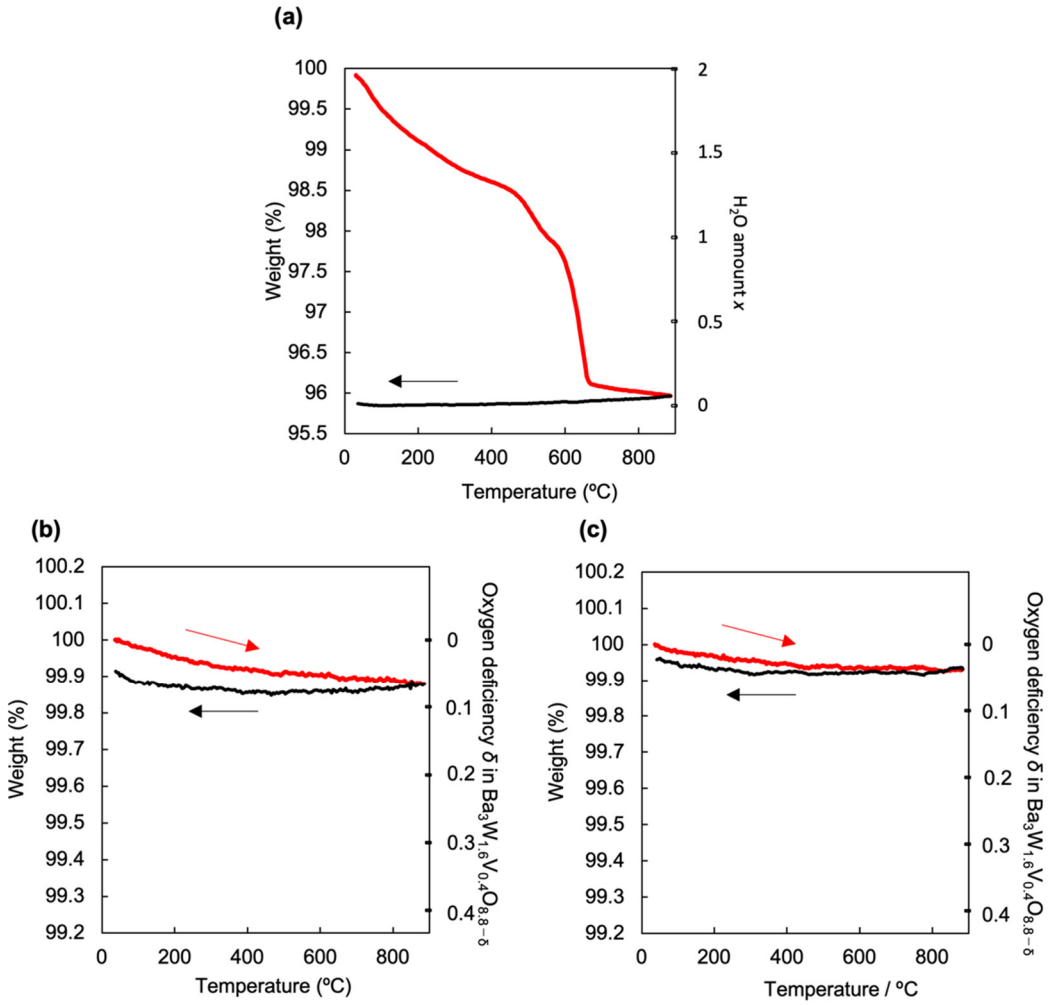

Figure S3. Thermogravimetric (TG) curves of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ in dry air at (a) 1st, (b) 2nd, and (c) 3rd cycles. Similar TG data were obtained also for $Ba_3WVO_{8.5}$.

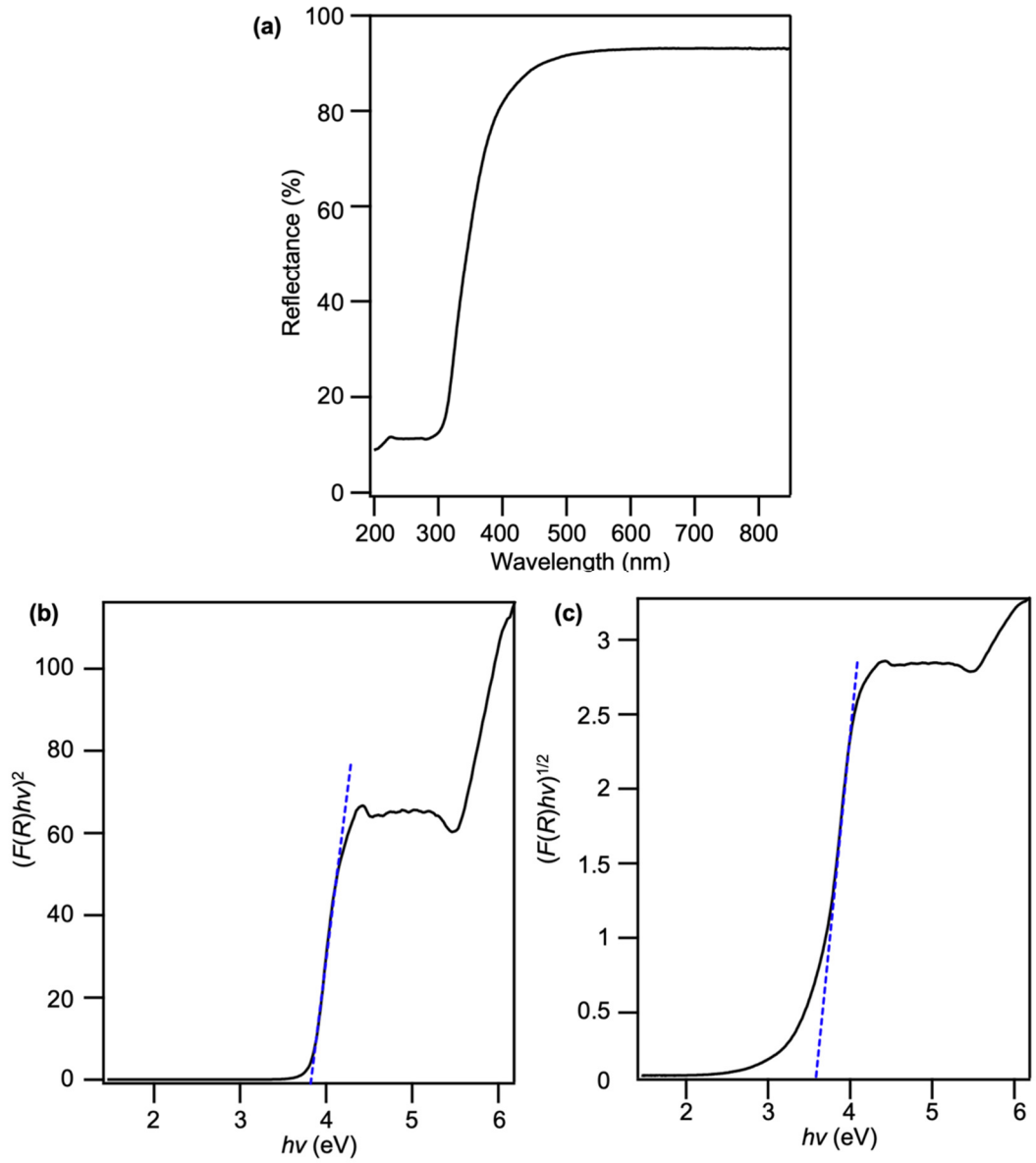

Figure S4. Diffuse reflectance spectrum and Tauc plots of $Ba_3W_{1.6}V_{0.4}O_{8.8}$. (a) Diffuse reflectance spectrum and Tauc plots for the (b) direct and (c) indirect band gaps of $Ba_3W_{1.6}V_{0.4}O_{8.8}$. Here $F(R)$ is the Kubelka-Munk function. The estimated bandgaps of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ were 3.84 and 3.56 eV assuming direct and indirect transitions, respectively. The direct and indirect band gaps were 3.86 and 3.25 eV, respectively, for the mother material $Ba_3WVO_{8.5}$.

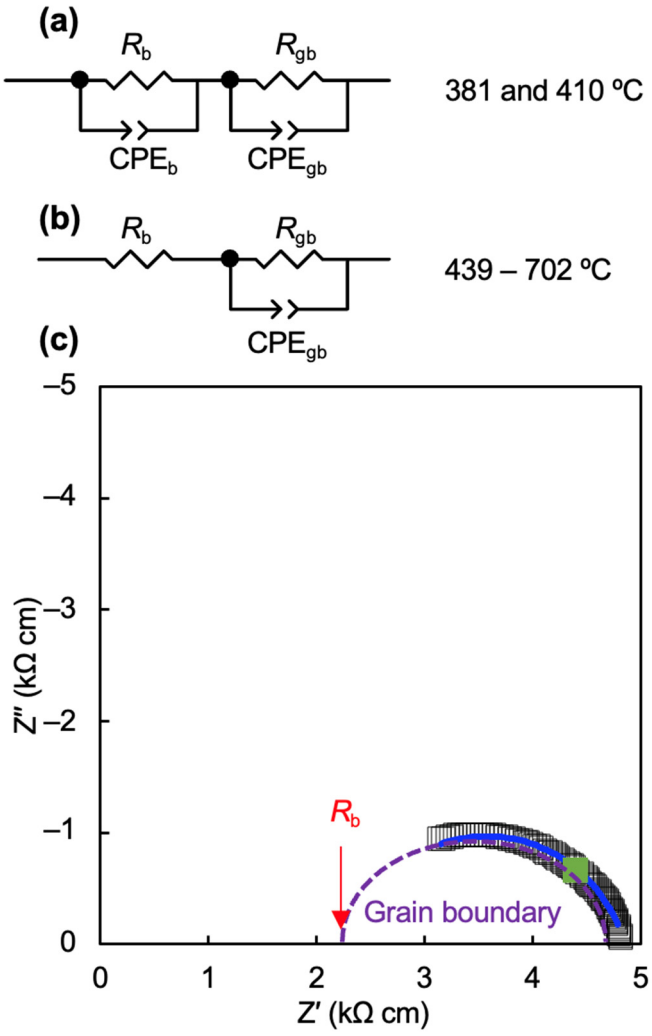

Figure S5. Equivalent circuits and complex impedance plots of $Ba_3W_{1.6}V_{0.4}O_{8.8}$. (a, b) Equivalent circuits used to model the impedance data of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ at 381–410 ºC (a) and 439–702 ºC (b). (c) Complex impedance plots of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ under dry air at 589 ºC.

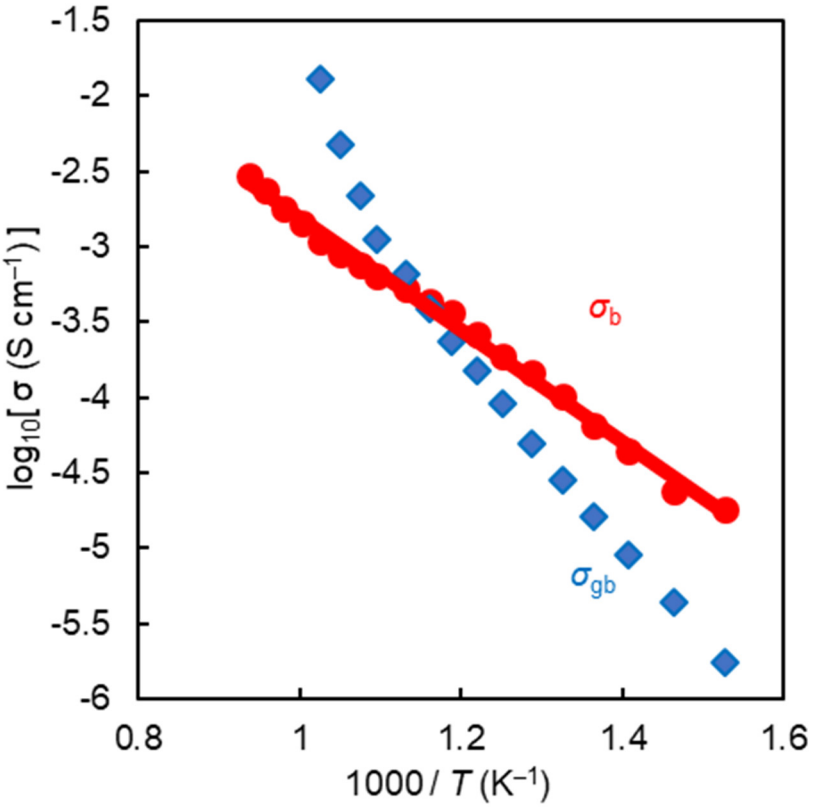

Figure S6. Arrhenius plots of bulk and grain boundary conductivities of $Ba_3W_{1.6}V_{0.4}O_{8.8}$. Arrhenius plots of bulk (σ_b) and grain boundary (σ_{gb}) conductivities of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ in dry air. The σ_b values at temperatures higher than 710 ºC were estimated using the semicircular sections in the Nyquist curves.

Table S1. Refined crystallographic parameters and reliability factors of the neutron-diffraction data of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ at 18 ºC.

Site / Atom label	Ba1	Ba2	W/V	O1	O2	O3
Atom	Ba	Ba	$W_{0.8}V_{0.2}$	O	O	O
g	1	1	1	1	0.662(2)	0.0678(5)
x	0	0	0	0.17431(5)	1/2	0.0721(6)
y	0	0	0	–0.17431(5)	0	0.0085(10)
z	0	0.20809(8)	0.39456(8)	0.10287(2)	0	0.32331(14)
U_{iso} or U_{eq} (Å^2)	0.0092(3)	0.0230(3)	0.0142(3)	0.01660(17)	0.0477(7)	0.0050(14)
U_{11} (Å^2)	0.0064(5)	0.0113(3)		0.0152(2)	0.0368(6)	
U_{22} (Å^2)	0.0064(5)	0.0113(3)		0.0152(2)	0.0784(15)	
U_{33} (Å^2)	0.0148(9)	0.0463(8)		0.0193(3)	0.0278(9)	
U_{12} (Å^2)	0.0032(2)	0.00566(18)		0.0102(3)	0.0392(7)	
U_{13} (Å^2)	0	0		–0.00065(17)	0.0170(5)	
U_{23} (Å^2)	0	0		0.00065(17)	0.0340(10)	
BVS	2.37	2.11	W^{6+}: 5.91, V^{5+}: 4.70	1.98	1.76	3.11

Crystal system: trigonal. Space group: $R\bar{3}m$ (No. 166, hexagonal setting). a = 5.81897(2) Å, c = 21.0057(2) Å. Number of formula units per unit cell: Z = 3.

$g(X, s)$: Occupancy factor of X atom at the s site. g(Ba; Ba1) = g(Ba; Ba2) = g($W_{0.8}V_{0.2}$; W/V) = g(O; O1) = 1. Linear constraints for occupancy factors: $9g$(O; O2) + $36g$(O; O3) = 7.5.

$U(X, s) = U(s) = U$: Atomic displacement parameter (ADP) of X atom at the s site. U_{iso}: Isotropic ADP. U_{eq}: Equivalent isotropic ADP.

BVS: Bond-valence sum values were calculated using the bond-valence parameters after Adams and Rao (2011) [4].

Reliability factors: R_{wp} = 5.142%, R_p = 3.778%, R_B = 4.744%, R_F = 3.943%. Goodness of Fit GoF = 11.092.

In a preliminary analysis, the refined occupancy factor of W, g(W; W/V) was equal to 0.8 within three estimated standard deviation, thus, the g(W; W/V) value was fixed to 0.8 in the final refinement. The weight fraction of hexagonal $Ba_3W_{1.6}V_{0.4}O_{8.8}$ phase was 99.6%.

Table S2. Refined crystallographic parameters and reliability factors of the neutron-diffraction data of $Ba_3WVO_{8.5}$ at 18 ºC.

Site / Atom label	Ba1	Ba2	W/V	O1	O2	O3
Atom	Ba	Ba	$W_{0.5}V_{0.5}$	O	O	O
g	1	1	1	1	0.415(2)	0.1046(5)
x	0	0	0	0.17350(8)	1/2	0.0499(12)
y	0	0	0	–0.17350(8)	0	1.02(3)
z	0	0.20586(8)	0.39185(12)	0.10196(3)	0	0.32614(12)
U_{iso} or U_{eq} (Å^2)	0.0147(4)	0.0187(3)	0.0044(5)	0.0180(2)	0.0669(16)	0.0324(16)
U_{11} (Å^2)	0.0108(6)	0.0178(4)		0.0161(2)	0.0593(16)	
U_{22} (Å^2)	0.0108(6)	0.0178(4)		0.0161(2)	0.085(3)	
U_{33} (Å^2)	0.0223(11)	0.0207(8)		0.0219(4)	0.057(2)	
U_{12} (Å^2)	0.0054(3)	0.0089(2)		0.0106(3)	0.0423(17)	
U_{13} (Å^2)	0	0		0.0013(2)	0.0294(12)	
U_{23} (Å^2)	0	0		–0.0013(2)	0.059(2)	
BVS	2.20	2.06	W^{6+}: 6.44, V^{5+}: 4.87	1.84	1.77	3.49

Crystal system: trigonal. Space group: $R\bar{3}m$ (No. 166, hexagonal setting). a = 5.81918(4) Å, c = 21.1336(4) Å. Number of formula units per unit cell: Z = 3.

$g(X, s)$: Occupancy factor of X atom at the s site. g(Ba; Ba1) = g(Ba; Ba2) = g($W_{0.5}V_{0.5}$; W/V) = g(O; O1) = 1. Linear constraints for occupancy factors: 9g(O; O2) + 36g(O; O3) = 7.5.

$U(X, s) = U(s) = U$: Atomic displacement parameter (ADP) of X atom at the s site. U_{iso}: Isotropic ADP. U_{eq}: Equivalent isotropic ADP.

BVS: Bond-valence sum values were calculated using the bond-valence parameters after Adams and Rao (2011) [4].

Reliability factors: R_{wp} = 5.074%, R_p = 3.943%, R_B = 4.724%, R_F = 3.713%. Goodness of Fit GoF = 10.439.

Table S3. Refined crystallographic parameters and reliability factors of the neutron-diffraction data of $Ba_3W_{1.6}V_{0.4}O_{8.8}$ at 800 ºC.

Site / Atom label	Ba1	Ba2	W/V	O1	O2	O3
Atom	Ba	Ba	$W_{0.8}V_{0.2}$	O	O	O
g	1	1	1	1	0.6650(16)	0.0688(4)
x	0	0	0	0.17630(8)	1/2	0.0721(11)
y	0	0	0	–0.17630(8)	0	0.0765(9)
z	0	0.20723(13)	0.39531(12)	0.10199(4)	0	0.3218(2)
U_{iso} or U_{eq} (Å^2)	0.0251(6)	0.0435(5)	0.0243(5)	0.0434(3)	0.1095(12)	0.0197(18)
U_{11} (Å^2)	0.0239(9)	0.0354(7)	0.0185(6)	0.0459(5)	0.0783(12)	
U_{22} (Å^2)	0.0239(9)	0.0354(7)	0.0185(6)	0.0459(5)	0.186(2)	
U_{33} (Å^2)	0.0275(14)	0.0596(14)	0.0359(16)	0.0386(6)	0.064(2)	
U_{12} (Å^2)	0.0119(4)	0.0177(3)	0.0093(3)	0.0367(6)	0.0930(14)	
U_{13} (Å^2)	0	0	0	0.0010(2)	0.0372(11)	
U_{23} (Å^2)	0	0	0	–0.0010(2)	0.075(2)	
BVS	2.37	2.11	W^{6+}: 5.90 V^{5+}: 4.70	1.98	1.76	3.11

Crystal system: trigonal. Space group: $R\bar{3}m$ (No. 166, hexagonal setting). a = 5.91775(4) Å, c = 21.2366(4) Å. Number of formula units per unit cell: Z = 3.

$g(X, s)$: Occupancy factor of X atom at the s site. g(Ba; Ba1) = g(Ba; Ba2) = g($W_{0.8}V_{0.2}$; W/V) = g(O; O1) = 1. Linear constraints for occupancy factors: 9g(O; O2) + 36g(O; O3) = 7.5.

$U(X, s) = U(s) = U$: Atomic displacement parameter (ADP) of X atom at the s site. U_{iso}: Isotropic ADP. U_{eq}: Equivalent isotropic ADP.

BVS: Bond-valence sum values were calculated using the bond-valence parameters after Adams and Rao (2011) [4].

Reliability factors: R_{wp} = 4.304%, R_p = 3.063%, R_B = 4.953%, R_F = 3.707%. Goodness of Fit GoF = 9.411.

Table S4. Refined crystallographic parameters and reliability factors of the neutron-diffraction data of $Ba_3WVO_{8.5}$ at 800 ºC.

Site / Atom label	Ba1	Ba2	W/V	O1	O2	O3
Atom	Ba	Ba	$W_{0.5}V_{0.5}$	O	O	O
g	1	1	1	1	0.435(7)	0.0961(18)
x	0	0	0	0.17585(10)	1/2	0.0684(12)
y	0	0	0	0.82413(10)	0	0.063(2)
z	0	0.20642(13)	0.3926(2)	0.10159(5)	0	0.3263(2)
U_{iso} or U_{eq} (Å^2)	0.0349(8)	0.0445(6)	0.0326(11)	0.0502(5)	0.125(6)	0.037(3)
U_{11} (Å^2)	0.0377(13)	0.0443(9)	0.0179(14)	0.0510(6)	0.100(3)	
U_{22} (Å^2)	0.0377(13)	0.0443(9)	0.0179(14)	0.0510(6)	0.198(13)	
U_{33} (Å^2)	0.0292(18)	0.0446(17)	0.062(3)	0.0484(7)	0.078(4)	
U_{12} (Å^2)	0.0189(6)	0.0222(4)	0.0090(7)	0.0386(8)	0.099(6)	
U_{13} (Å^2)	0	0	0	0.0018(3)	0.044(3)	
U_{23} (Å^2)	0	0	0	–0.0018(3)	0.088(6)	
BVS	2.07	1.86	W^{6+}: 6.21 V^{5+}: 4.78	1.77	1.63	3.09

Crystal system: trigonal. Space group: $R\bar{3}m$ (No. 166, hexagonal setting). a = 5.90973(9) Å, c = 21.3120(8) Å. Number of formula units per unit cell: Z = 3.

$g(X, s)$: Occupancy factor of X atom at the s site. g(Ba; Ba1) = g(Ba; Ba2) = g($W_{0.8}V_{0.2}$; W/V) = g(O; O1) = 1. Linear constraints for occupancy factors: 9g(O; O2) + 36g(O; O3) = 7.5.

$U(X, s) = U(s) = U$: Atomic displacement parameter (ADP) of X atom at the s site. U_{iso}: Isotropic ADP. U_{eq}: Equivalent isotropic ADP.

BVS: Bond-valence sum values were calculated using the bond-valence parameters after Adams and Rao (2011) [4].

Reliability factors: R_{wp} = 3.294%, R_p = 2.515%, R_B = 4.882%, R_F = 4.831%. Goodness of Fit GoF = 4.220.

Supplementary Note: Influence of $BaWO_4$ impurity on the electrical conductivity of $Ba_3W_{1.6}V_{0.4}O_{8.8}$

In the literature, the $BaWO_4$ phase is reported to be a p-type electronic conductor.[5] We have not observed the p-type electronic conduction in the oxygen partial pressure dependence of electrical conductivity (Fig. 2a in the text), thus, the influence of $BaWO_4$ impurity phase on the electrical conductivity of the $x = 0.6$ sample is negligible.

References

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