Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

The Crystal Structure and Electrical Properties of the Oxide Ion Conductor $Ba_3WNbO_{8.5}$

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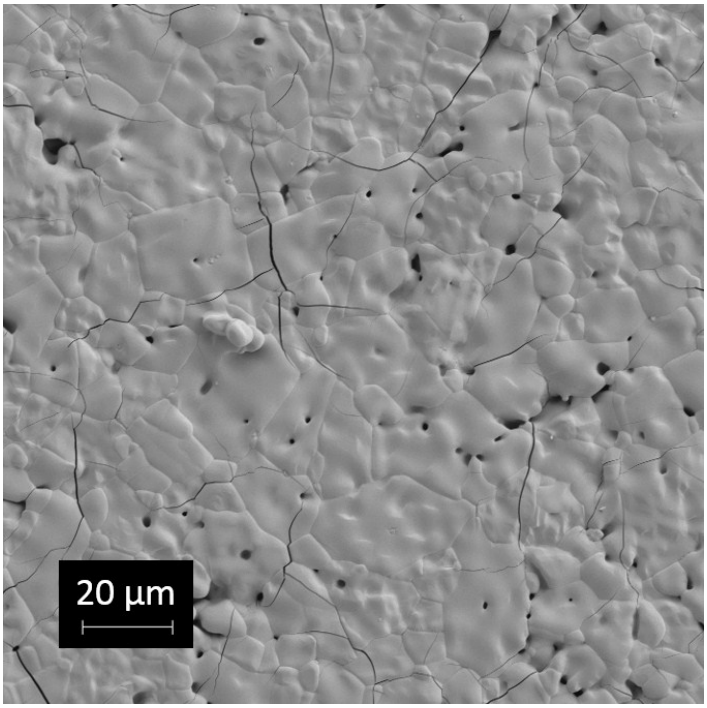
a



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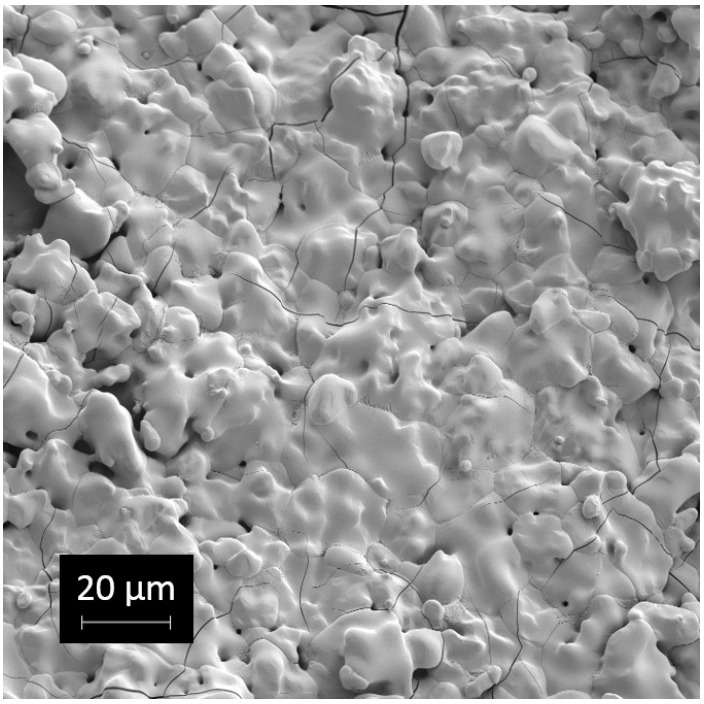

Figure S1 SEM micrographs of the surface (**a**) and section (b) of a pellet of $Ba_3WNbO_{8.5}$

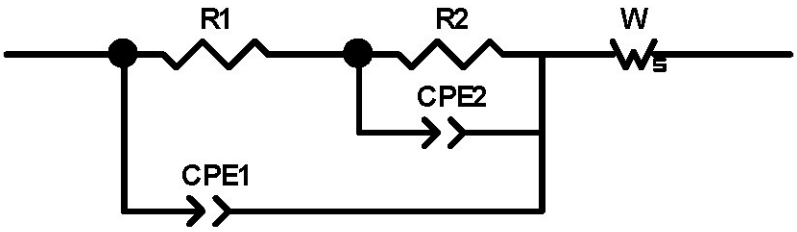

Figure S2 Equivalent circuit used to model the impedance data. The same equivalent circuit is reported in reference 1. R indicates a resistor and CPE a constant phase element. R1 and R2 represent the bulk and grain boundary respectively.

Reference

1. H. Zhang, A.Suresh, C. B. Carter and B. A. Wilhite, *Solid State Ionics*, 2014, **266**, 58-67.

Table S1. Refined atomic parameters for $Ba_3WNbO_{8.5}$ from the Rietveld fit of the neutron powder diffraction data recorded on the Polaris diffractometer.

Atom	Site	x	y	z	Occupancy	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
Ba(1)	3*a*	0	0	0	1	0.0005(5)	0.0005(5)	0.0053(9)	0.0002(3)	0	0
Ba(2)	6*c*	0	0	0.21005(9)	1	0.0143(4)	0.0143(4)	0.0168(10)	0.0071(2)	0	0
W(1)	6*c*	0	0	0.39288(10)	0.387(9)	0.0047(3)	0.0047(3)	0.0271(10)	0.0024(2)	0	0
Nb(1)	6*c*	0	0	0.39288(10)	0.428(9)	0.0047(3)	0.0047(3)	0.0271(10)	0.0024(2)	0	0
W(2)	3*b*	0	0	0.5	0.23(2)	0.022(3)	0.022(3)	0.40(2)	0.0110(13)	0	0
Nb(2)	3*b*	0	0	0.5	0.14(2)	0.022(3)	0.022(3)	0.40(2)	0.0110(13)	0	0
O(1)	18*h*	0.17444(8)	0.82556(8)	0.10596(4)	1	0.0167(3)	0.0167(3)	0.0240(5)	0.0134(4)	0.0030(2)	-0.0030(2)
O(2)	9*e*	0.5	0	0	0.758(3)	0.0175(6)	0.0299(10)	0.0207(10)	0.0150(5)	0.0113(5)	0.0226(9)
O(3)	18*h*	0.050(2)	0.010(4)	0.3209(11)	0.038(2)	0.025(6)[a]					

[a] U_{iso} (Å)

Table S2. Selected bond lengths calculated from the Rietveld refinement of powder neutron diffraction data of $Ba_3MoNbO_{8.5}$ and $Ba_3WNbO_{8.5}$.

Bond-length (Å)	$Ba_3MoNbO_{8.5}$	$Ba_3WNbO_{8.5}$
Ba(1)-O(1)	2.8080(6)	2.8427(8)
Ba(1)-O(2)	2.96372(2)	2.92844(5)
Ba(1)-O(3)	3.015(5)	3.170(7)
Ba(2)-O(1)	2.799(2)/2.997(2)	2.812(2)/2.9520(3)
Ba(2)-O(2)	3.180(2)	3.092(2)
Ba(2)-O(3)	2.447(3)	2.38(2)
M(1)-O(1)	1.8337(8)	1.884(1)
M(1)-O(2)	2.2065(8)	2.103(1)
M(1)-O(3)	1.766(4)	1.59(2)
M(2)-O(1)	2.1260(6)	2.0550(9)
D*	0	0.32

*D is the displacement of the M(1) atom closer to the O(2)/O(3) sites, in respect to its equilibrium position in $Ba_3MoNbO_{8.5}$.

Table S3. Selected bond angles calculated from the Rietveld refinement of powder neutron diffraction data of $Ba_3MoNbO_{8.5}$ and $Ba_3WNbO_{8.5}$.

Angle (°)	$Ba_3MoNbO_{8.5}$	$Ba_3WNbO_{8.5}$
O(1)-M(1)-O(1) (α)	102.83(5)	95.66(9)
O(1)-M(1)-O(3) (β)	114.8(2)	125.2(4)
O(1)-M(1)-O(2) (γ)	85.51(2)	87.91(2)
O(1)-M(1)-O(2) (γ)	166.34(7)	174.67(11)
O(2)-M(1)-O(2) (δ)	84.38(4)	88.26(7)
O(1)-M(2)-O(1)	84.79(2)	85.58(3)
O(1)-M(2)-O(1)	95.213(2)	94.43(3)

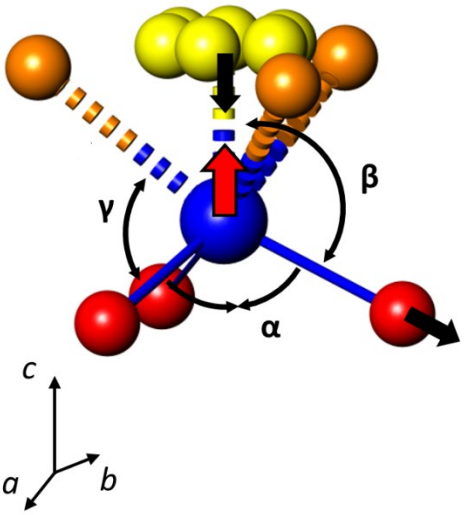

Fig. S3 A superimposition of the coordination of the M(1)–$O(1)_3O(3)$ tetrahedra and the M(1)–$O(1)_3O(2)_3$ octahedra. The black arrows show the modifications of the bond lengths and angles for $Ba_3WNbO_{8.5}$ from the values found for $Ba_3MoNbO_{8.5}$. The red arrow represents the average M(1) displacement.