Supporting Information for

Synthesis and Symmetry of Perovskite Oxynitride $CaW(O,N)_3$

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Methods

X-ray photoelectron spectroscopy (XPS) measurements were taken using the Thermo Scientific ESCALAB 250 Xi instrument using charge compensation and a spot size of 500 μm. All element-specific regions were scanned with a with a pass energy of 50 eV. Charge shift was done to the C-C peak at 284.8 eV and carbon signal was used to correct the oxygen composition[1]. Fits were made to the observed data using CasaXPS software. Mean free paths, instrument transmission functions, and Thermo Scientific values for relative scattering factor were used to convert integrated area into atomic composition estimates.

Figures and Tables

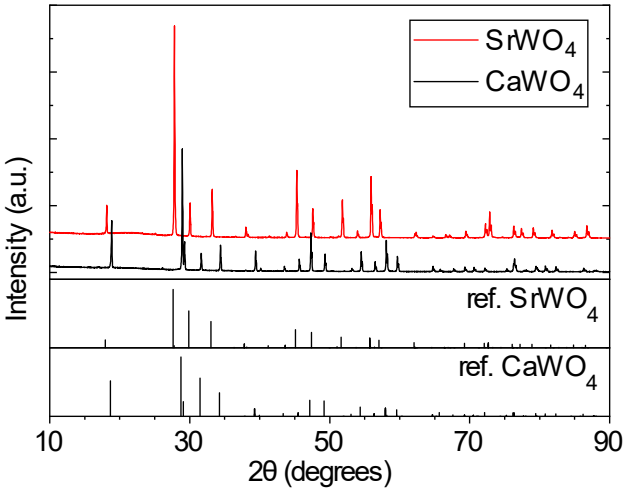

Fig. S1: XRD patterns for the scheelite $SrWO_4$ and $CaWO_4$ intermediate materials used for synthesis of $SrW(O,N)_3$ and $CaW(O,N)_3$ compared with reference patterns[2, 3].

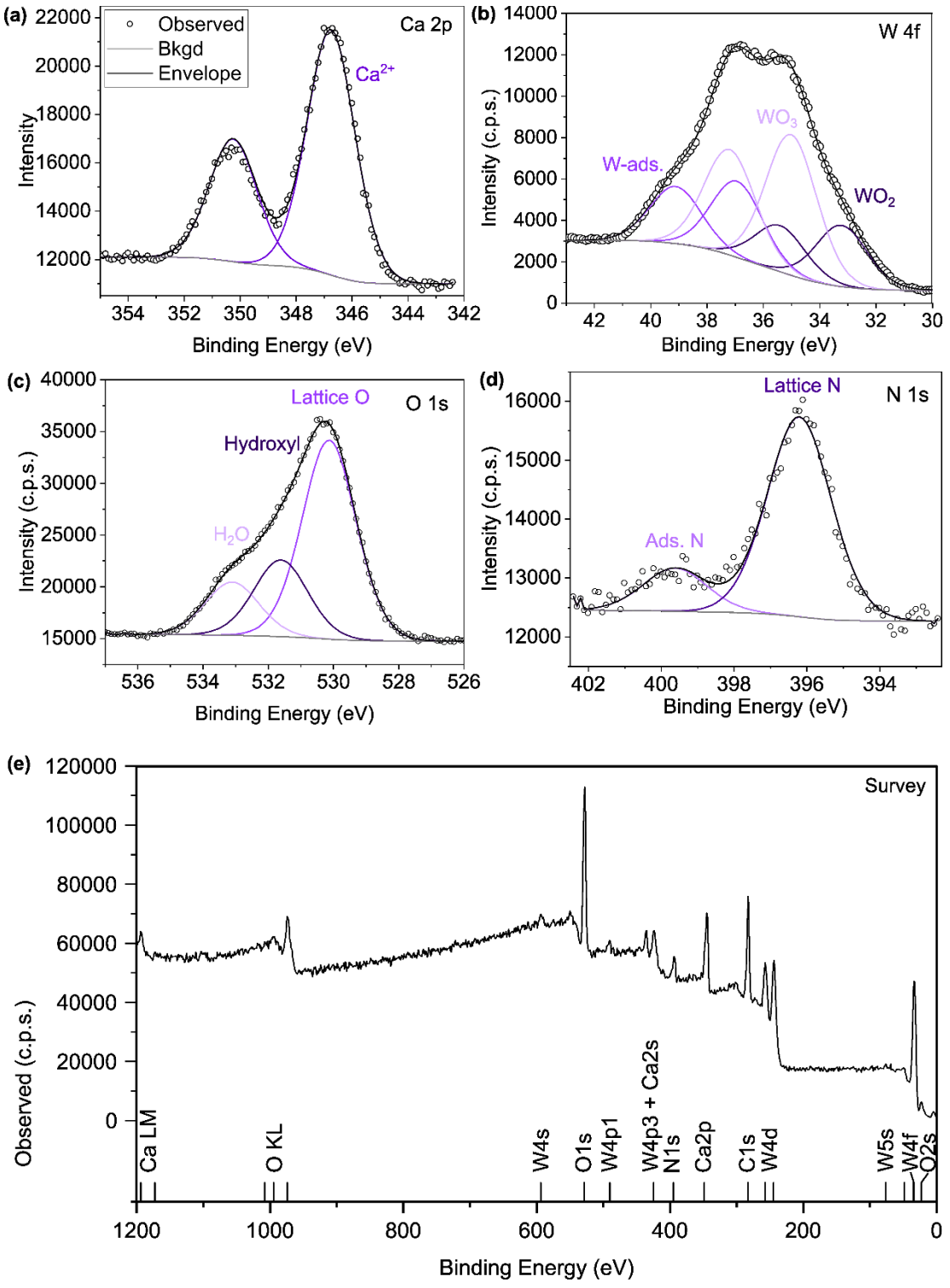

Fig. S2: X-ray photoelectron spectra of the (a) Ca 2p, (b) W 4f, (c) O 1s, and (d) N 1s regions. All peaks in the (e) survey scan correspond to expected elements.

Table S1. Surface composition of $CaW(O,N)_3$ measured by XPS. Adventitious carbon signal is not included, but is used to correct for surface oxygen species. All uncertainties are approximately 10% of the reported value.

Ca (at%)	W (at%)	O (at%)	N (At%)
19	15	47	19

Table S2. Bulk anion composition reported from combustion analysis with provided uncertainty and calculated O,N stoichiometry.

	wt% N	**±**	**wt% H**	**±**	**O range**	**N range**
$CaW(O,N)_3$	8.35	0.15	0.13	0.15	1.4–1.7	1.3–1.6
$SrW(O,N)_3$	7.38	0.15	0.18	0.15	1.3–1.7	1.3–1.7

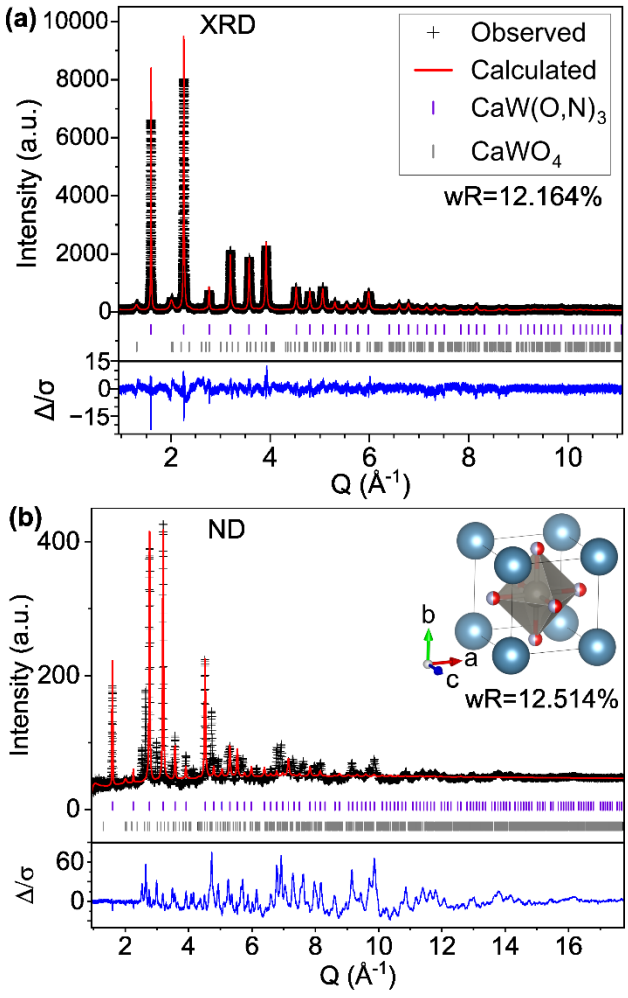

Fig. S3. Rietveld refinement of $CaW(O,N)_3$ (a) synchrotron XRD and (b) ND patterns to structural model C-I with cubic $Pm\bar{3}m$ symmetry predicted by the tolerance ratio provides an inadequate fit to ND.

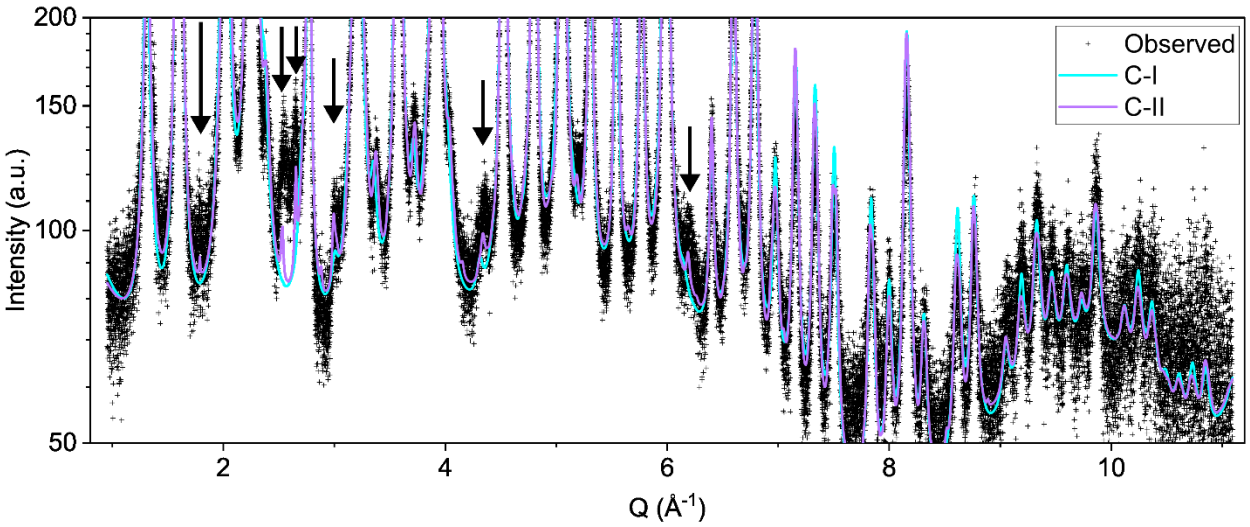

Fig. S4. Comparison of the fit of models C-I and C-II to the experimental XRD pattern. Several peaks, identified with arrows, are completely unmatched by the cubic C-I model and/or are fit significantly better by the orthorhombic C-II model.

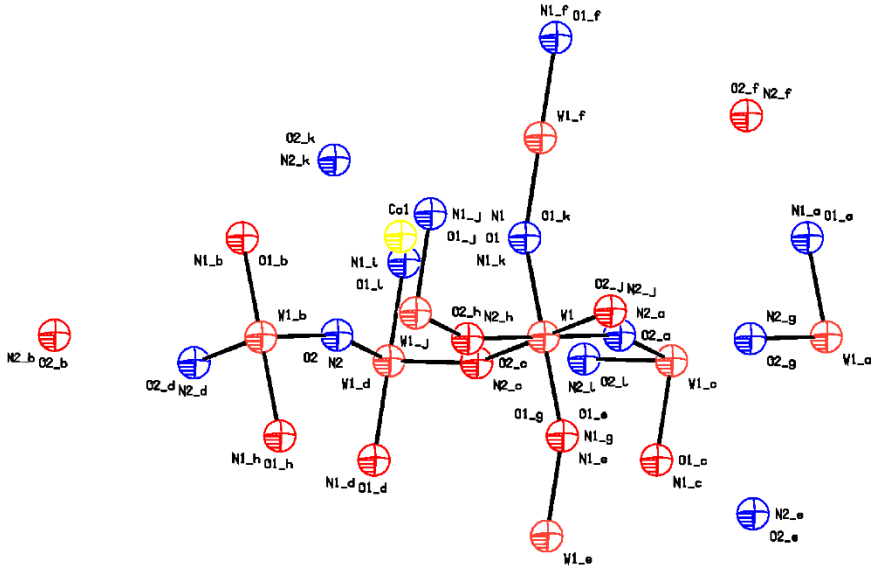

Fig. S5. Line drawing of $CaW(O,N)_3$ model C-II with atomic positions listed in Table 2. Image generated from PLATON program.

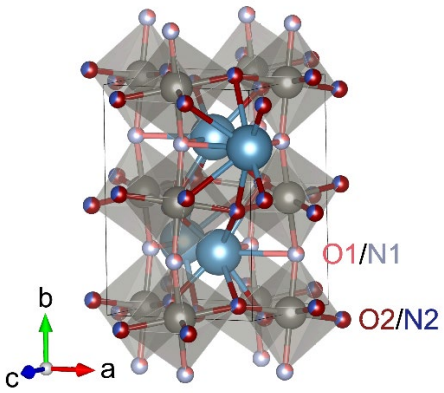

Fig. S6. Crystal structure schematic of model C-II with anion sites O1/N1 and O2/N2 labeled.

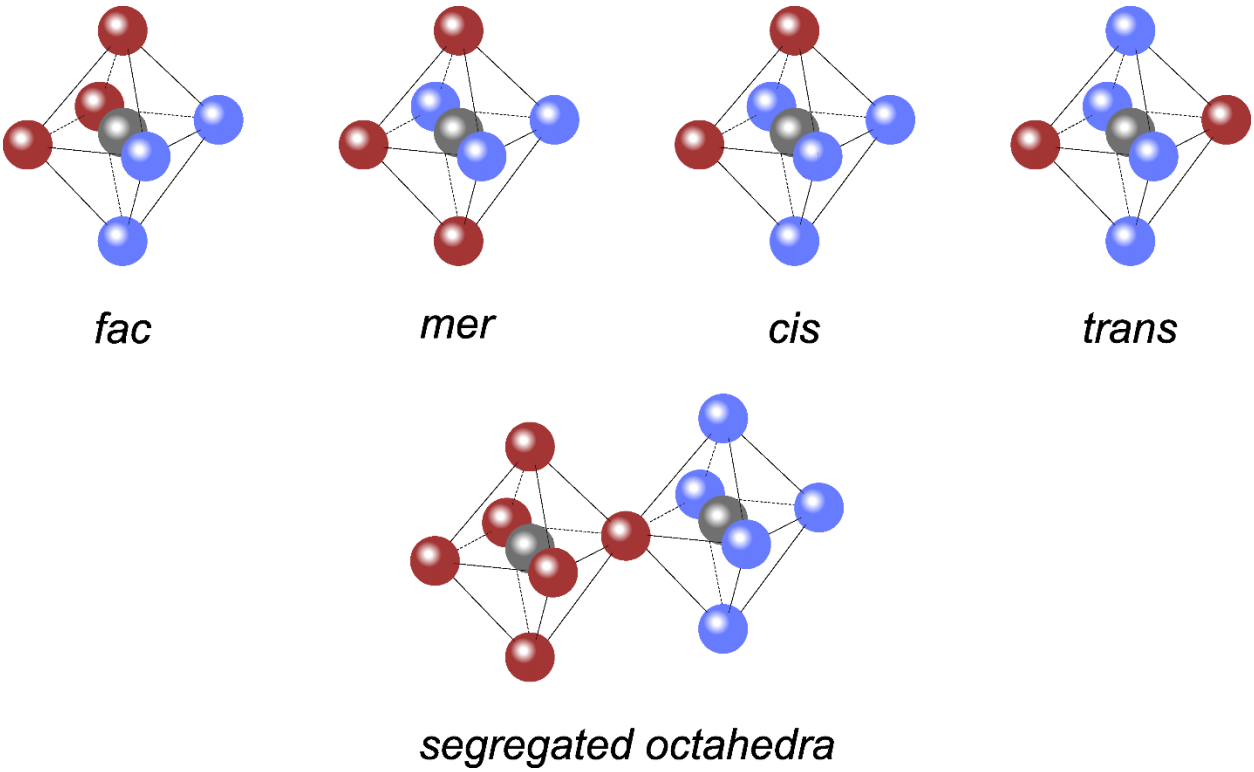

Fig. S7. Possible configurations of anions in WX_6 octahedra labeled with their corresponding names.

Table S3. Comparison of weighted residuals from Rietveld refinement of orthorhombic *Pnma* structural model with and without fixed anion site occupancy for overall stoichiometry $CaWO_{1.5}N_{1.5}$.

Model	Anion site occupancy	Overall wR (%)	XRD wR (%)	ND wR (%)
C-II	allowed to vary	5.029	9.536	2.781
C-III	fixed @ 0.5	5.041	9.528	2.817

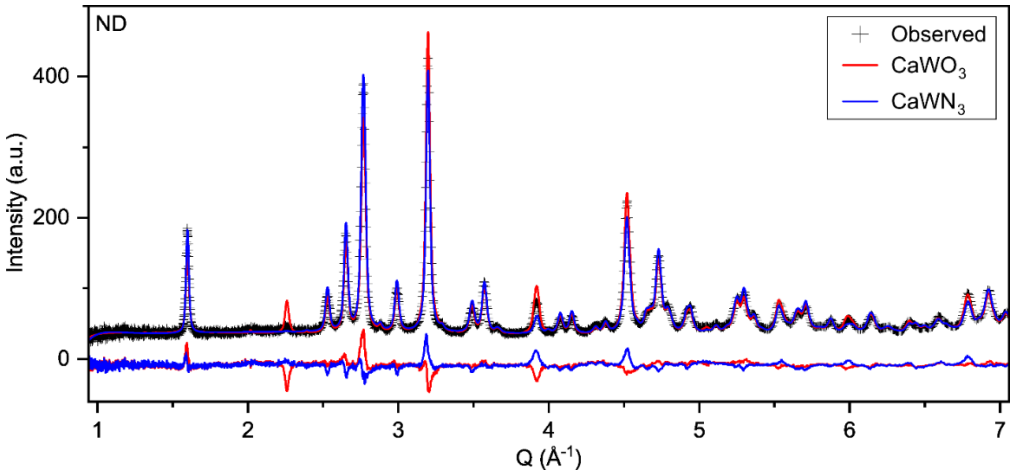

Fig. S8. Overlaid Rietveld refinements of $CaW(O,N)_3$ ND pattern using all-O and all-N models (C-VI and C-VII, respectively). Plotted residuals identify where each composition mismatches the observed data.

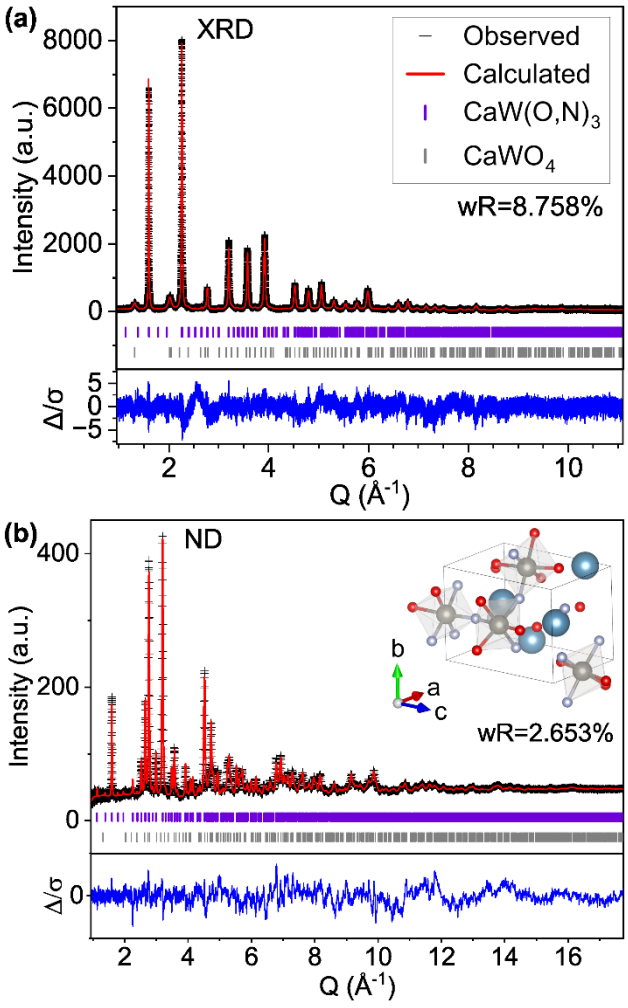

Fig. S9. Rietveld refinement of $CaW(O,N)_3$ (a) synchrotron XRD and (b) ND patterns to the best fit 20-atom DFT-determined structure with *P1* symmetry and disordered anions (model C-VIII, structure F).

Table S4: Structural parameters for $CaW(O,N)_3$ from Rietveld refinement of diffraction patterns with a 60-atom providing the best fit to diffraction data (model C-IX, structure C). Atomic positions in Table S4.

Formula	$CaWO_{1.5}N_{1..5}$
S.G. #	1
S.G.	*P1*
Crystal system	Triclinic
a	5.5635(1) Å
b	7.87236(15) Å
c	16.6013(3) Å
α	90.203(5) °
β	90.124(2) °
γ	89.7797(8) °
Volume	727.16(2) $Å^3$

Type	**Occ.**	**Uiso**
Ca	1	0.0057(7)
W	0.982(2)	0.0145(1)
O	1	0.0023(3)
N	0.880(5)	0.0103(4)

Table S5: Atomic position, occupancy, and atomic displacement parameters for model C-IX.

Name	x	y	z	Occ.	Uiso	Name	x	y	z	Occ.	Uiso
Ca0	-0.020(5)	0.710(4)	0.319(1)	1	0.0057(7)	N30	0.273(5)	0.513(3)	0.426(2)	0.880(5)	0.0103(4)
Ca1	0.001(6)	0.769(4)	0.665(2)	1	0.0057(7)	N31	0.278(5)	0.951(3)	0.435(2)	0.880(5)	0.0103(4)
Ca2	-0.004(6)	0.734(4)	0.003(2)	1	0.0057(7)	N32	0.484(4)	0.742(3)	0.315(2)	0.880(5)	0.0103(4)
Ca3	0.487(6)	0.251(4)	0.165(2)	1	0.0057(7)	N33	0.493(4)	0.749(3)	0.651(1)	0.880(5)	0.0103(4)
Ca4	0.468(6)	0.253(4)	0.836(2)	1	0.0057(7)	N34	0.531(5)	0.261(3)	0.019(1)	0.880(5)	0.0103(4)
Ca5	0.479(7)	0.264(4)	0.499(2)	1	0.0057(7)	N35	0.718(5)	0.013(3)	0.577(1)	0.880(5)	0.0103(4)
Ca6	0.524(5)	0.781(4)	0.845(2)	1	0.0057(7)	N36	0.726(5)	0.470(4)	0.236(2)	0.880(5)	0.0103(4)
Ca7	0.502(6)	0.738(4)	0.167(2)	1	0.0057(7)	N37	0.715(5)	0.019(4)	0.908(2)	0.880(5)	0.0103(4)
Ca8	0.500(5)	0.801(3)	0.485(1)	1	0.0057(7)	N38	0.786(4)	0.549(3)	0.736(2)	0.880(5)	0.0103(4)
Ca9	0.989(6)	0.246(5)	0.330(2)	1	0.0057(7)	N39	0.784(5)	0.977(3)	0.740(2)	0.880(5)	0.0103(4)
Ca10	0.964(6)	0.264(4)	0.665(2)	1	0.0057(7)	N40	1.001(5)	0.759(3)	0.853(2)	0.880(5)	0.0103(4)
Ca11	0.956(5)	0.246(4)	1.002(2)	1	0.0057(7)	N41	0.998(5)	0.757(3)	0.186(2)	0.880(5)	0.0103(4)
W12	0.006(3)	0.498(2)	0.168(1)	0.982(2)	0.0145(1)	O42	0.003(5)	0.247(3)	0.143(1)	1	0.0023(3)
W11	-0.006(4)	0.005(2)	0.500(1)	0.982(2)	0.0145(1)	O43	0.035(4)	0.256(3)	0.806(1)	1	0.0023(3)
W14	-0.005(3)	0.990(2)	0.168(1)	0.982(2)	0.0145(1)	O44	0.212(5)	0.463(3)	0.601(2)	1	0.0023(3)
W15	0.016(3)	0.512(2)	0.499(1)	0.982(2)	0.0145(1)	O45	0.201(5)	0.032(3)	0.266(2)	1	0.0023(3)
W16	0.496(4)	0.009(2)	0.999(1)	0.982(2)	0.0145(1)	O46	0.224(5)	0.472(3)	0.930(2)	1	0.0023(3)
W17	0.499(4)	0.501(2)	0.001(1)	0.982(2)	0.0145(1)	O47	0.284(5)	0.541(4)	0.760(2)	1	0.0023(3)
W18	0.487(3)	0.485(2)	0.343(1)	0.982(2)	0.0145(1)	O48	0.282(5)	0.979(4)	0.761(2)	1	0.0023(3)
W19	0.496(4)	0.997(2)	0.338(1)	0.982(2)	0.0145(1)	O49	0.491(5)	0.758(3)	0.980(2)	1	0.0023(3)
W20	0.499(3)	0.514(2)	0.666(1)	0.982(2)	0.0145(1)	O50	0.540(5)	0.266(3)	0.689(1)	1	0.0023(3)
W21	0.489(3)	0.995(2)	0.671(1)	0.982(2)	0.0145(1)	O51	0.505(5)	0.237(3)	0.361(1)	1	0.0023(3)
W22	1.000(3)	1.000(3)	0.834(1)	0.982(2)	0.0145(1)	O52	0.701(4)	0.491(3)	0.570(1)	1	0.0023(3)
W23	1.008(4)	0.510(2)	0.829(1)	0.982(2)	0.0145(1)	O53	0.702(4)	0.033(3)	0.235(2)	1	0.0023(3)
N24	-0.011(5)	0.238(3)	0.487(1)	0.880(5)	0.0103(4)	O54	0.715(5)	0.474(3)	0.903(1)	1	0.0023(3)
N25	0.221(4)	0.030(3)	0.596(2)	0.880(5)	0.0103(4)	O55	0.811(4)	0.957(3)	0.072(2)	1	0.0023(3)
N26	0.237(4)	0.454(3)	0.257(1)	0.880(5)	0.0103(4)	O56	0.795(4)	0.542(3)	0.068(2)	1	0.0023(3)
N27	0.212(5)	0.030(4)	0.933(2)	0.880(5)	0.0103(4)	O57	0.773(5)	0.531(3)	0.407(2)	1	0.0023(3)
N28	0.339(3)	0.993(3)	0.103(1)	0.880(5)	0.0103(4)	O58	0.788(5)	0.965(4)	0.408(2)	1	0.0023(3)
N29	0.286(5)	0.540(3)	0.096(2)	0.880(5)	0.0103(4)	O59	0.999(5)	0.746(3)	0.522(2)	1	0.0023(3)

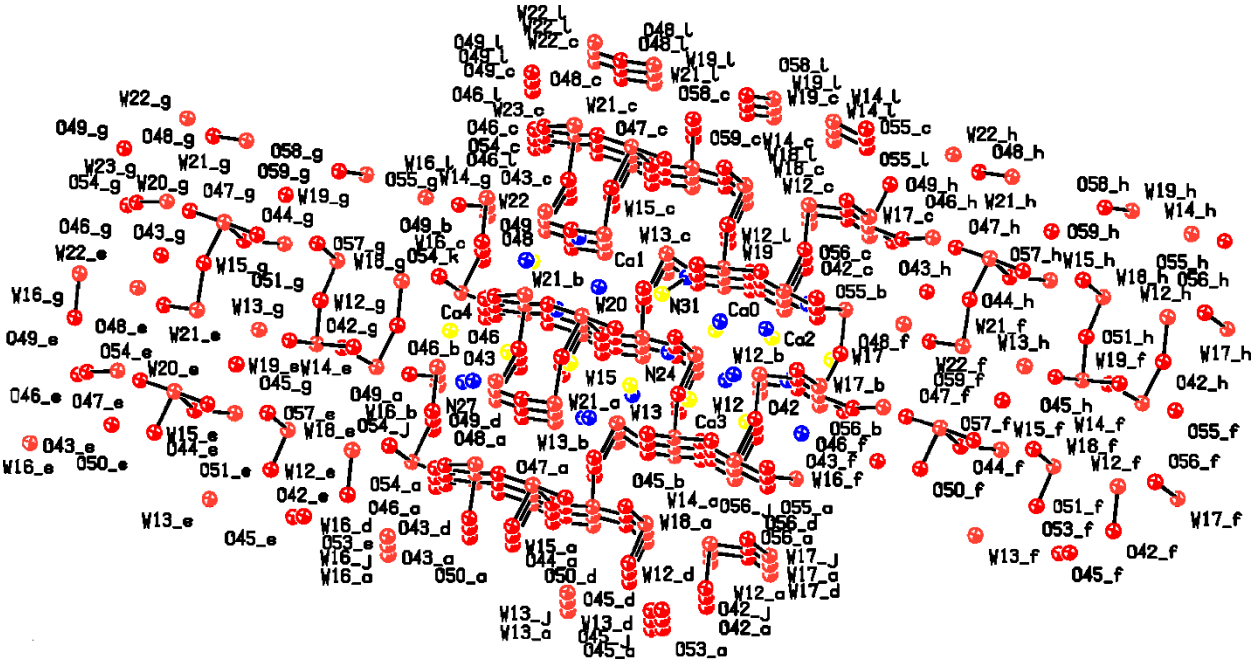

Fig. S10: Line drawing of model C-IX with labeled atoms corresponding to atomic positions in Table S4. Image generated from PLATON program.

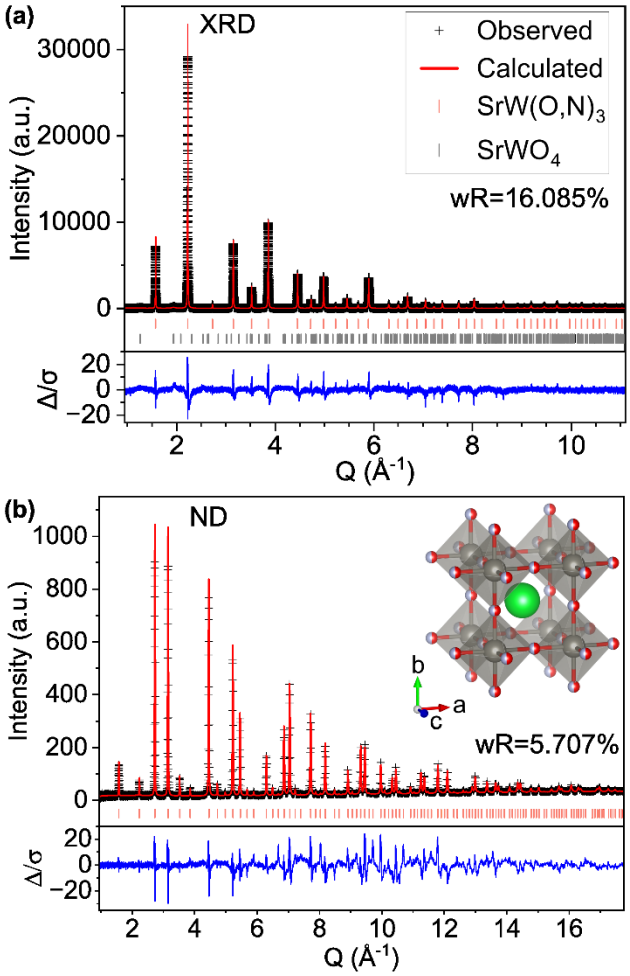

Fig. S11: Rietveld refinement of $SrW(O,N)_3$ (a) synchrotron XRD and (b) ND patterns to the reported $Pm\bar{3}m$ structure with disordered anions (model S-I).

Table S6: Structural parameters from Rietveld refinement of diffraction patterns with model S-I.

Formula			$SrWO_{1.5}N_{1.5}$		
Space group number			221		
Space group symbol			$Pm\bar{3}m$		
Crystal system			Cubic		
a			3.98697(1) Å		
Volume			63.376(1) Å^3		
Site	**x**	**y**	**z**	**Occ.**	**Uiso**
Sr	0.5	0.5	0.5	1	0.01073(8)
W	0	0	0	1	0.01218(6)
O1	0.5	0	0	0.5	0.00600(3)
N1	-	-	-	0.5	-

Table S7: Unit cell information and lattice parameters for model S-II.

Formula	$SrWO_{1.5}N_{1.5}$
S.G. #	1
S.G.	*P1*
Crystal system	Triclinic
a	5.64456(6) Å
b	7.97340(7) Å
c	11.26568(8) Å
α	90.019(2) °
β	90.1053(6) °
γ	89.9492(7) °
Volume	507.025(4) $Å^3$

Table S8: Atomic position, occupancy, and atomic displacement parameters for model S-II.

Site	x	y	z	Occ.	Uiso
N1	0.747(9)	0.751(7)	0.121(4)	0.956(1)	0.0060(4)
N2	0.249(7)	0.25(1)	0.127(3)	0.956(1)	0.0060(4)
N3	0.753(7)	0.257(8)	0.122(3)	0.956(1)	0.0060(4)
N4	1.005(6)	0.504(8)	0.256(4)	0.956(1)	0.0060(4)
N5	0.731(5)	0.755(7)	0.367(3)	0.956(1)	0.0060(4)
N6	0.246(7)	0.756(8)	0.378(4)	0.956(1)	0.0060(4)
N7	0.747(7)	0.257(9)	0.376(3)	0.956(1)	0.0060(4)
N8	0.502(8)	0.51(1)	0.504(3)	0.956(1)	0.0060(4)
N9	0.504(7)	0.01(1)	0.505(3)	0.956(1)	0.0060(4)
N10	0.248(7)	0.753(8)	0.628(3)	0.956(1)	0.0060(4)
N11	-0.006(8)	1.00(1)	0.748(4)	0.956(1)	0.0060(4)
N12	0.248(7)	0.259(7)	0.873(4)	0.956(1)	0.0060(4)
O13	0.24(1)	0.76(1)	0.120(5)	0.967(5)	0.0058(8)
O14	-0.01(1)	-0.01(1)	0.253(7)	0.967(5)	0.0058(8)
O15	0.25(1)	0.25(1)	0.377(6)	0.967(5)	0.0058(8)
O16	0.254(9)	0.26(1)	0.630(5)	0.967(5)	0.0058(8)
O17	0.75(1)	0.75(1)	0.621(5)	0.967(5)	0.0058(8)
O18	0.75(1)	0.25(1)	0.622(5)	0.967(5)	0.0058(8)
O19	0.99(1)	0.51(2)	0.751(6)	0.967(5)	0.0058(8)
O20	0.74(1)	0.75(1)	0.871(5)	0.967(5)	0.0058(8)
O21	0.74(1)	0.26(1)	0.866(5)	0.967(5)	0.0058(8)
O22	0.241(9)	0.751(9)	0.868(5)	0.967(5)	0.0058(8)
O23	0.497(9)	1.01(1)	0.994(5)	0.967(5)	0.0058(8)
O24	0.505(8)	0.51(1)	1.006(4)	0.967(5)	0.0058(8)
Sr25	-0.005(9)	1.00(1)	0.002(4)	0.977(1)	0.0106(4)
Sr26	0.50(1)	0.50(1)	0.249(6)	0.977(1)	0.0106(4)
Sr27	0.50(1)	0.00(1)	0.250(6)	0.977(1)	0.0106(4)
Sr28	0.001(8)	0.01(1)	0.497(4)	0.977(1)	0.0106(4)
Sr29	-0.006(8)	0.51(1)	0.501(4)	0.977(1)	0.0106(4)
Sr30	0.505(9)	0.51(1)	0.751(6)	0.977(1)	0.0106(4)
Sr31	0.496(9)	0.01(1)	0.755(5)	0.977(1)	0.0106(4)
Sr32	-0.009(9)	0.51(1)	0.998(4)	0.977(1)	0.0106(4)
W33	0.488(4)	0.754(7)	0.002(3)	1	0.0137(1)
W34	0.494(4)	0.254(8)	0.001(3)	1	0.0137(1)
W35	1.001(4)	0.259(5)	0.248(3)	1	0.0137(1)
W36	1.000(4)	0.756(6)	0.250(3)	1	0.0137(1)
W37	0.494(4)	0.756(7)	0.501(3)	1	0.0137(1)
W38	0.497(4)	0.256(7)	0.499 (3)	1	0.0137(1)
W39	0.003(4)	0.759(5)	0.749(3)	1	0.0137(1)
W40	-0.007(4)	0.253(5)	0.751(3)	1	0.0137(1)

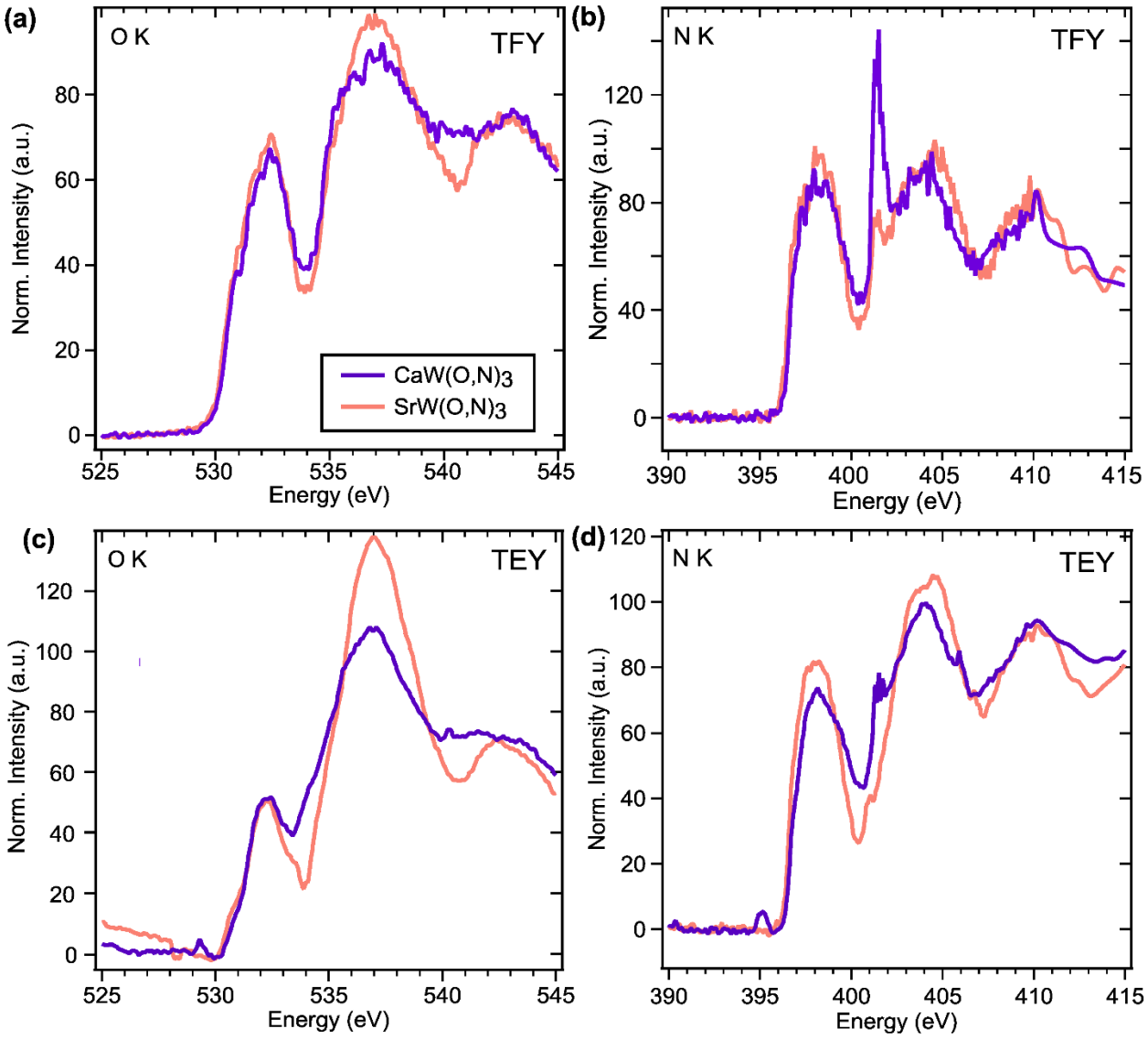

Fig. S12: X-ray absorption spectra of $CaW(O,N)_3$ and $SrW(O,N)_3$ at the O and N K-edges measured using total fluorescence yield (TFY) and total electron yield (TEY). (a) O K-edge TFY, (b) N K-edge TFY, (c) O K-edge TEY, (b) N K-edge TEY. Intensities are area-normalized between 528–545 eV for O K-edge and 394–410 eV for N K-edge.

References

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2. S. P. Culver, M. J. Greaney, A. Tinoco and R. L. Brutchey, *Dalton Transactions*, 2015, **44**, 15042-15048.
3. R. M. Hazen, L. W. Finger and J. W. E. Mariathasan, *Journal of Physics and Chemistry of Solids*, 1985, **46**, 253-263.