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Supplementary material

Study on the thermal conversion of scheelite-type ABO_4 into perovskite-type $AB(O,N)_3$

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Figures

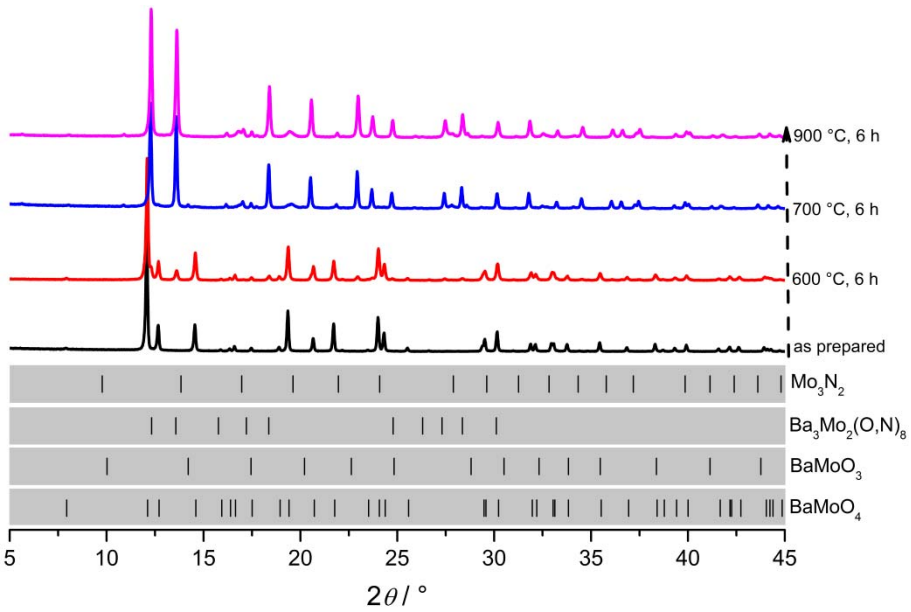

Figure S 1 XRD patterns of $BaMoO_4$ after heating at 600, 700 and 900 ^{0}C under an ammonia flow for 6 hours.

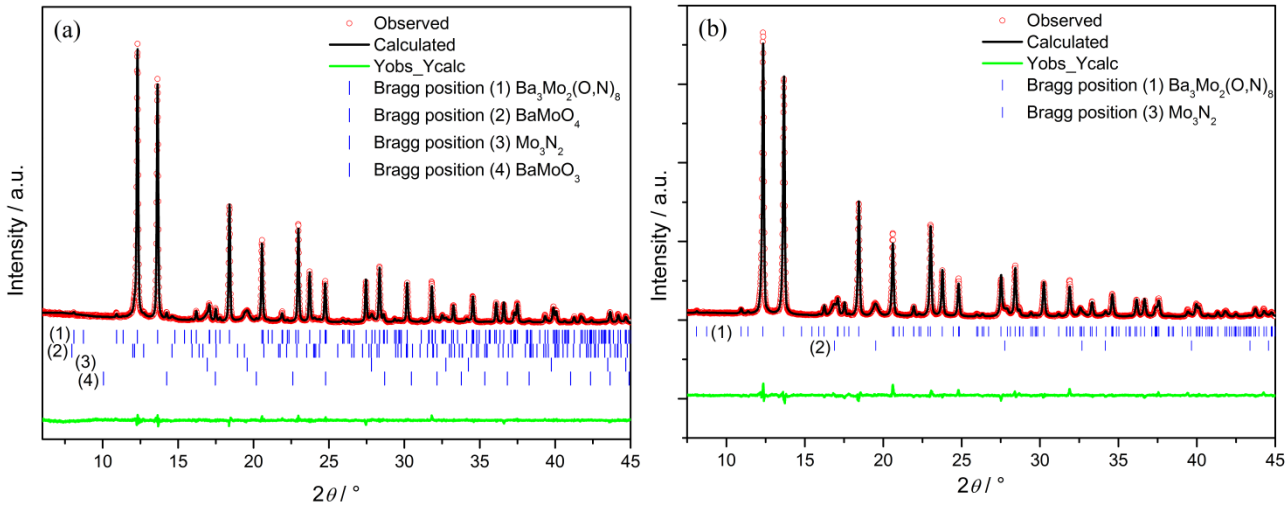

Figure S 2 Rietveld refinement of the X-ray powder diffraction patterns of the samples obtained from the ammonolysis of $BaMoO_4$ (a) 700 ^{0}C for 6 hours and (b) 900 ^{0}C for 6 hours. Blue tick marks are Bragg peak positions of related phase (bottom); (a) (1) $Ba_3Mo_2(O,N)_8$, (2) $BaMoO_4$, (3) Mo_3N_2 and (4) $BaMoO_3$; (b) (1) $Ba_3Mo_2(O,N)_8$ and (2) Mo_3N_2. Green line at the bottom denotes the difference intensities between the observed and calculated profiles. Table S1 summarizes the results of the structure refinement.

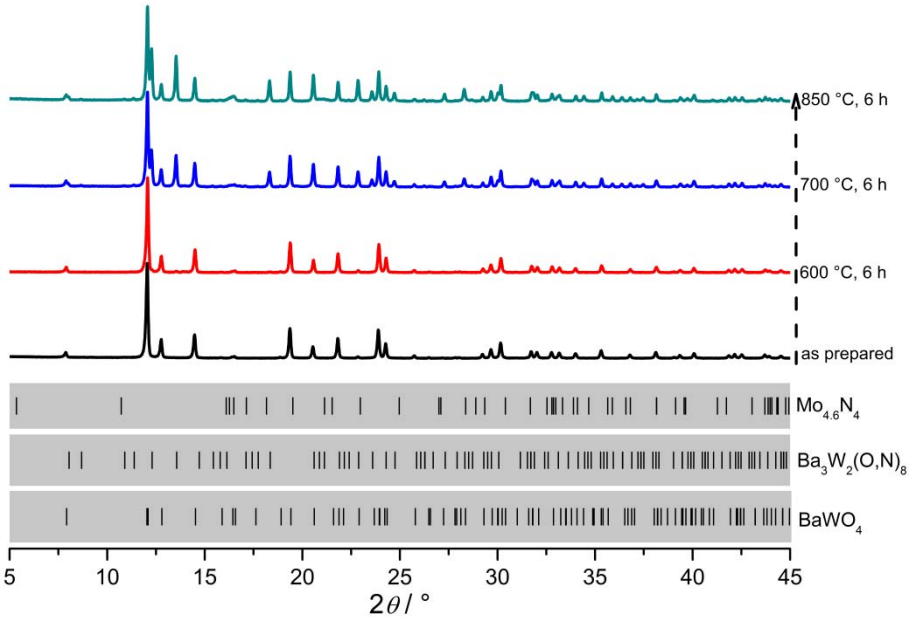

Figure S 3 XRD patterns of $BaWO_4$ after heating at 600, 700 and 850 ^{0}C under an ammonia flow for 6 hours.

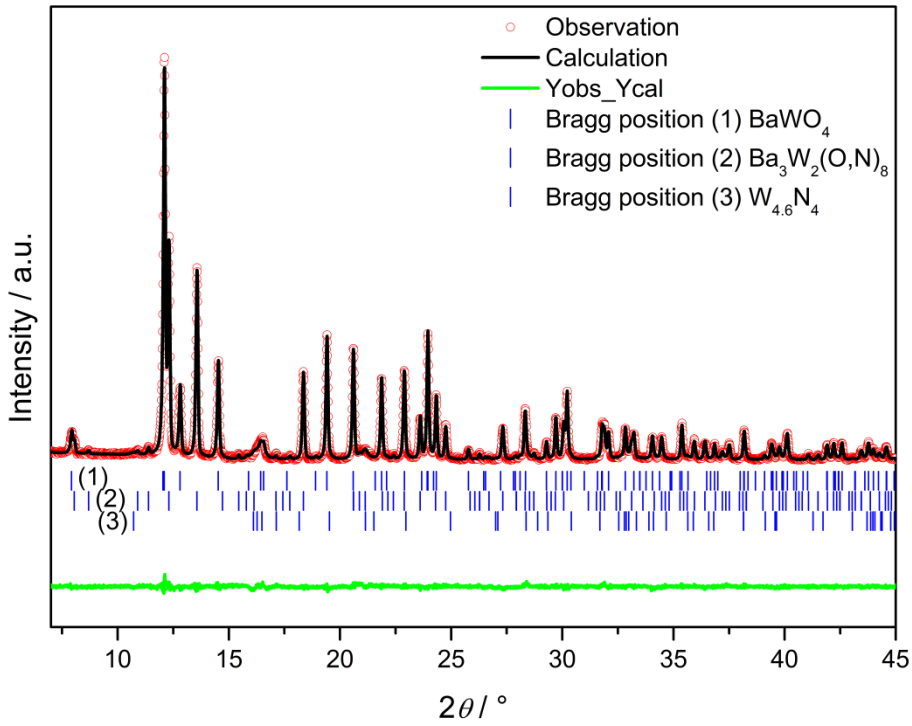

Figure S 4 Rietveld refinement of the X-ray powder diffraction pattern of the sample obtained from the ammonolysis of $BaWO_4$ at 850 ^{0}C for 6 hours. Blue tick marks are Bragg peak positions of related phase (bottom) as (1) $BaWO_4$, (2) $Ba_3W_2(O,N)_8$ and (3) $W_{4.6}N_4$. Green line at the bottom denotes the difference intensities between the observed and calculated profiles. Error! Reference source not found. summarizes the results of the structure refinement.

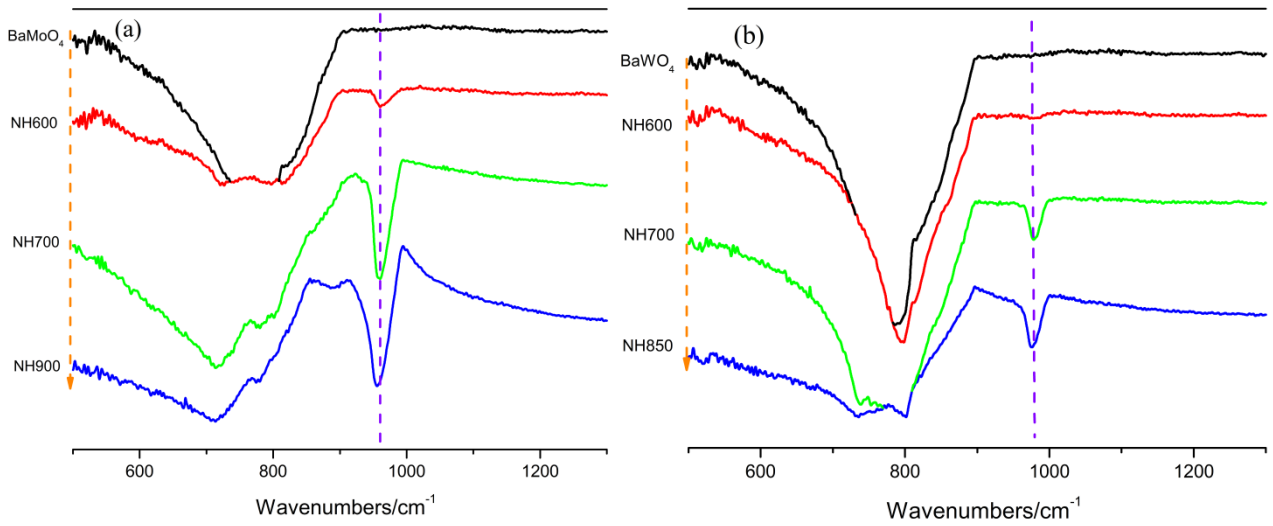

Figure S 5 FTIR spectra of the as-synthesized scheelite oxides and the corresponding materials after their ammonolysis at different temperatures: (a) $BaMoO_4$; (b) $BaWO_4$. NHx00 denotes the thermal treatment at different temperatures under ammonia flow for 6 hours.

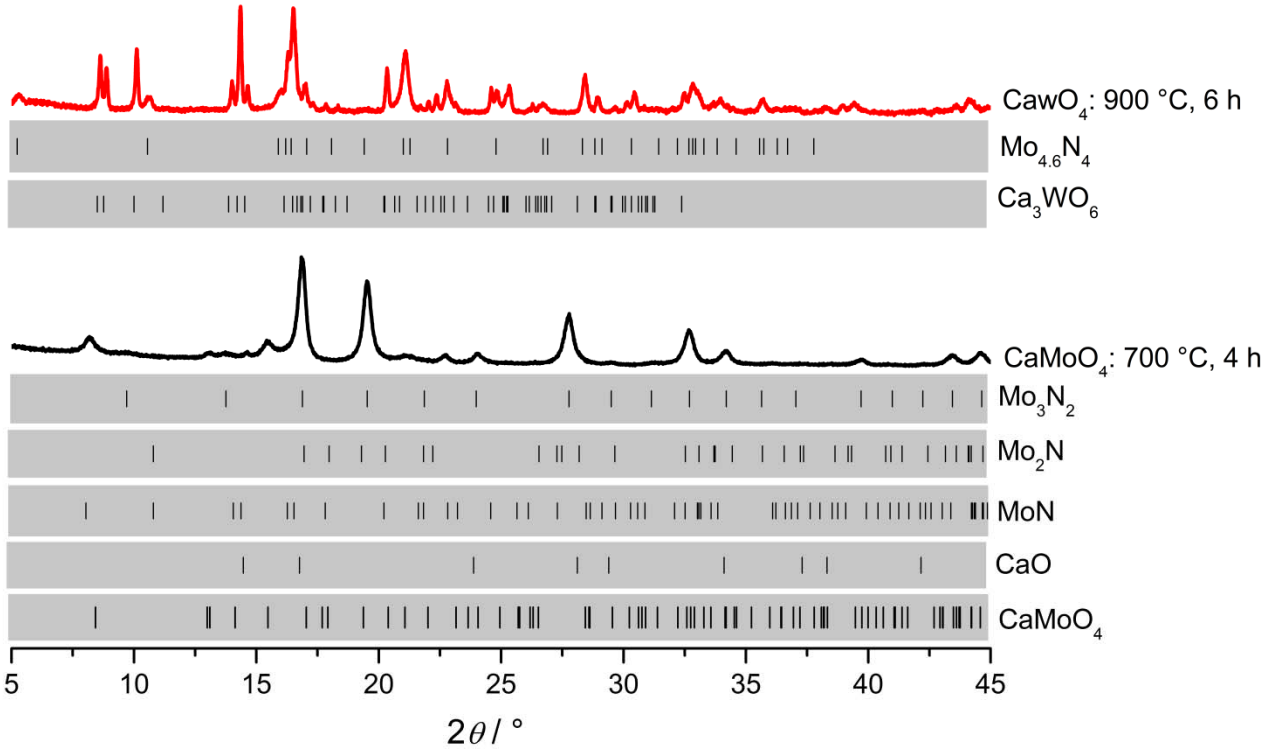

Figure S 6 XRD patterns of $CaMoO_4$ and $CaWO_4$ after ammonolysis at 700 for 4 h (bottom) and 900 ^{0}C for 6 h (top).

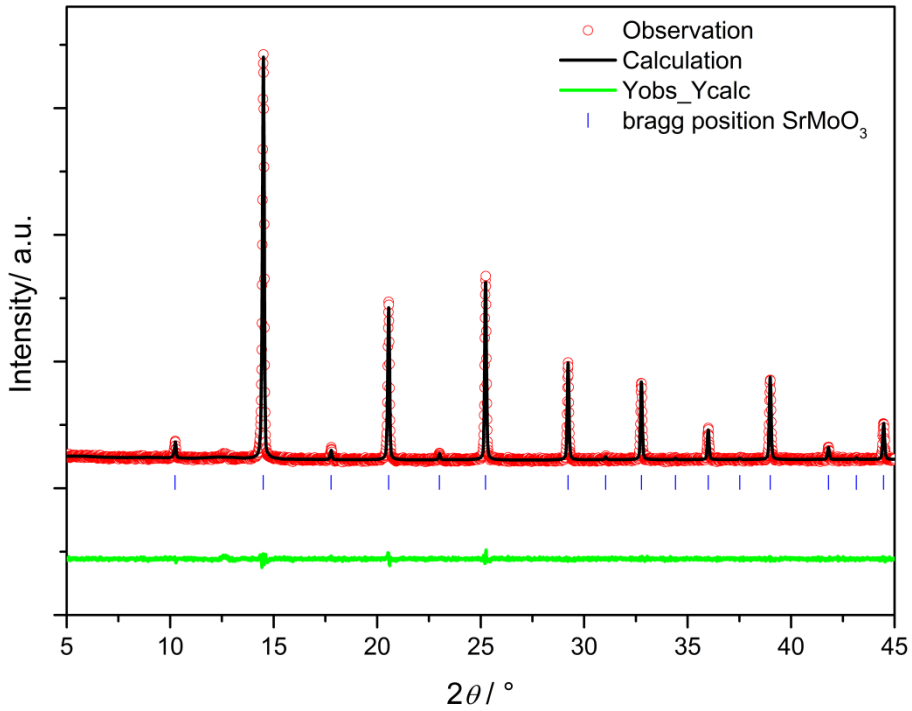

Figure S 7 Rietveld patterns of the X-ray powder diffraction data of the sample obtained upon reduction of the $SrMoO_4$ at 900 °C for 6 h. Blue tick marks are Bragg peak positions of related phase as $SrMoO_3$. Green line at the bottom denotes the difference intensities between the observed and calculated profiles. Error! Reference source not found. summarizes the results of the structure refinement.

Tables

Table S 1 Phase composition of the samples obtained via ammonolysis of $BaMoO_4$ at 700 and 900 ^{0}C for 6 hours from Rietveld refinement of the XRD patterns. [a]

Specimen	$Ba_3Mo_2(O,N)_8$ (*R-3m*, Nr. 166, *Z*=3)	$BaMoO_4$ (*I 41/a*, Nr. 88, *Z*=4)	Mo_3N_2 (*Pm-3m*, Nr. 221, *Z*=1)	$BaMoO_3$ (*Pm-3m*, Nr. 221, *Z*=1)
NH700 (Figure S 2 a)	79.93 a=5.9579(2) c=21.4662(6)	10.72 a=5.5830(14) c=12.8117(59)	9.35 a=4.1708(6)	0.01 a=4.0489(6)
NH900 (Figure S 2 b)	85.94 a=5.9670(3) c=21.4812(10)	/	14.06 a=4.1839(6)	/

[a] Fraction (wt%) and lattice parameter a,b,c [Å]

Table S 2 Phase composition of the samples obtained via ammonolysis of $BaWO_4$ at 850 ^{0}C for 6 hours from Rietveld refinement of the XRD patterns. [a]

Specimen	$BaWO_4$ (*I 41/a*, Nr. 88, *Z*=4)	$Ba_3W_2(O,N)_8$ (*R-3m*, Nr. 166, *Z*=3)	$W_{4.6}N_4$ (P63/mmc, Nr. 194, *Z*=1)
NH850 (Figure S 4)	54.79 a=5.6111(2) c=12.7188(5)	34.24 a=6.0057(2) c=21.4469(9)	10.97 a=2.8943(7) c=15.1899(55)

[a] Fraction (wt%) and lattice parameter a,b,c [Å]

Table S 3 Crystal structure data of $SrMoO_{3.61}N_{0.39}$, $SrMoO_4$ and $SrMoO_3$

Specimens and parameters		$SrMoO_{3.61(3)}N_{0.39(3)}$	$SrMoO_4$	$SrMoO_3$
S.G.		*I 41/a*, Nr. 88	*I 41/a*, Nr. 88	*P m-3m*, Nr. 221
Z		4	4	1
a,b, Å		5.3947(2)	5.4032(2)	3.9763(1)
c, Å		12.0367(5)	12.0412(4)	/
Sr	x, y, z	0.0,0.25,0.625	0.0,0.25,0.625	0.5, 0.5, 0.5
	Biso, Å^2	0.210(70)	0.461(100)	0.472(47)
	Occ.	1	1	1
Mo	x, y, z	0.0,0.25,0.125	0.0,0.25,0.125	0.0, 0.0, 0.0
	Biso, Å^2	0.383(68)	0.587(95)	0.148(42)
	Occ.	1	1	1
O/N	x	0.24078(78)	0.24042(105)	0.5
	y	0.11411(69)	0.11602(88)	0.0
	z	0.04267(29)	0.04162(38)	0.0
	Biso, Å^2	-0.369(111)	0.380(161)	0.578(102)
	Occ.	3.61/0.39[a]	4	3

[a]: Not refined

Table S 4 The lattice parameters of $Ba_3W_2O_6N_2$ and $W_{4.6}N_4$ based on our as-synthesized sample via ammonolysis of $BaWO_4$ at 850 ^{0}C for 6 hours and Reference obtained by Rietveld refinement

	Lattice parameter based on our experiments		Lattice parameter from Reference	
	a=b	c	a=b	c
$Ba_3W_2O_6N_2$	6.0057 (2)	21.4469 (9)	6.0083 (6)[1]	21.4637 (6)[1]
$W_{4.6}N_4$	2.8943 (7)	15.1899 (55)	2.89[2]	15.3[2]

Table S 5 The oxygen and nitrogen content in weight percent of $BaMoO_4$ and $BaWO_4$ after thermal ammonolysis under different temperature. NHx00 denotes the different thermal ammonolysis temperatures.

Samples	$BaMoO_4$_NH600	$BaMoO_4$_NH700	$BaMoO_4$_NH900	$BaWO_4$_NH600	$BaWO_4$_NH700	$BaWO_4$_NH850
Oxygen wt%	18.3(0.166)	12.77(0.153)	11.54(0.174)	15.88(0.33)	13.58(0.276)	12.17(0.257)
Nitrogen wt%	0.788(0.002)	5.014(0.033)	5.476(0.021)	0.045(0.01)	8.74(0.297)	9.435(0.64)

Table S 6 The oxygen and nitrogen content in weight percent of $SrMoO_4$ and $SrWO_4$ after thermal ammonolysis under different temperature and holding time

Sample	Oxygen wt%	Nitrogen wt%
$SrMoO_4$_NH400_4H	24.830(24)	0
$SrMoO_4$_NH600_4H	22.260(25)	2.230(3)
$SrMoO_4$_NH700_4H	14.790(18)	5.542(10)
$SrMoO_4$_NH700_12H	13.940(270)	6.318(104)
$SrMoO_4$_NH700_24H	12.750(215)	7.187(83)
$SrMoO_3$_NH700_4H	19.180(178)	1.386(25)
$SrWO_4$_NH400_4H	18.310(220)	0.017(15)
$SrWO_4$_NH600_4H	18.740(123)	0.095(11)
$SrWO_4$_NH700_4H	17.130(153)	1.002(6)
$SrWO_4$_NH900_6H	8.547(375)	6.373(130)
$SrWO_4$_NH900_12H	8.114(170)	7.006(110)
$SrWO_4$_NH900_24H	7.977(25)	7.148(70)

Table S 7 Thermodynamic cycles for the determination of the enthalpies of formation of $SrMoO_4$ and $SrMoO_{1.96}N_{1.04}$ relative to elementary components

Reaction	**Enthalpy (kJ/mol)**
(1) $SrMoO_4$ (s, 25 C) = SrO (soln, 701 C) + MoO_3 (soln, 701 C)	161.8 ± 1.5
(2) $SrMoO_{1.96}N_{1.04}$ (s, 25 C) + $1.02O_2$ (g, 701 C) = SrO (soln, 701 C) + MoO_3 (soln, 701 C) + $0.52N_2$ (g, 701 C)	-291.9 ± 2.3
(3) SrO (s, 25 C) = SrO (soln, 701 C)	-135.8 ± 2.5
(4) MoO_3 (s, 25 C) = MoO_3 (soln, 701 C)	72.8 ± 0.6
(5) O_2 (g, 25 C) = O_2 (g, 701 C)	21.8 ± 0
(6) N_2 (g, 25 C) = N_2 (g, 701 C)	20.6 ± 0
(7) Sr (s, 25 C) + 0.5 O_2 (g, 25 C) = SrO (s, 25 C)	-591.3 ± 1
(8) Mo (s, 25 C) + $1.5O_2$ (g, 25 C) = MoO_3 (s, 25 C)	-745.2 ± 0.4
(9) Sr (s, 25 C) + Mo (s, 25 C)+ 2O2 (g, 25 C) = $SrMoO_4$ (s, 25 C)	
$\mathbf{\Delta H_9 = -\Delta H_1 + \Delta H_3 + \Delta H_4 + \Delta H_7 + \Delta H_8}$	-1561.3 ± 3.1
(10) Sr (s, 25 C) + Mo (s, 25 C)+ $0.98O_2$ (g, 25 C) + $0.52N_2$ (g, 25 C) = $SrMoO_{1.96}N_{1.04}$ (s, 25 C)	
$\mathbf{\Delta H_{10} = -\Delta H_2 + \Delta H_3 + \Delta H_4 - 1.02\ \Delta H_5 + 0.52\Delta H_6 + \Delta H_7 + \Delta H_8}$	-1119.124 ± 3.6

Table S 8 Thermodynamic cycles for the determination of the enthalpies of formation of $SrWO_4$ and $SrWO_{1.5}N_{1.5}$ relative to elementary components

Reaction	**Enthalpy (kJ/mol)**		
(1) $SrWO_4$ (s, 25 C) = SrO (soln, 701 C) + WO_3 (soln, 701 C)	162.8	±	1.5
(2) $SrWO_{1.5}N_{1.5}$ (s, 25 C) + 1.25O_2 (g, 701 C) = SrO (soln, 701 C) + WO_3 (soln, 701 C) + 0.75N_2 (g, 701 C)	-537.2	±	1.9
(3) SrO (s, 25 C) = SrO (soln, 701 C)	-135.8	±	2.5
(4) WO_3 (s, 25 C) = WO_3 (soln, 701 C)	91.7	±	1.3
(5) O_2 (g, 25 C) = O_2 (g, 701 C)	21.8	±	0
(6) N_2 (g, 25 C) = N_2 (g, 701 C)	20.6	±	0
(7) Sr (s, 25 C) + 0.5 O_2 (g, 25 C) = SrO (s, 25 C)	-591.3	±	1
(8) W (s, 25 C) + 1.5O_2 (g, 25 C) = WO_3 (s, 25 C)	-842.9	±	0.8
(9) Sr (s, 25 C) + W (s, 25 C)+ 2O_2 (g, 25 C) = $SrWO_4$ (s, 25 C)			
$\mathbf{\Delta H_9 = -\Delta H_1 + \Delta H_3 + \Delta H_4 + \Delta H_7 + \Delta H_8}$	-1641.2	±	3.8
(10) Sr (s, 25 C) + W (s, 25 C)+ 0.75O_2 (g, 25 C) + 0.75N_2 (g, 25 C) = $SrWO_{1.5}N_{1.5}$ (s, 25 C)			
$\mathbf{\Delta H_{10} = -\Delta H_2 + \Delta H_3 + \Delta H_4 - 1.25\ \Delta H_5 + 0.75\Delta H_6 + \Delta H_7 + \Delta H_8}$	-952.9	±	4.3

Table S 9 The enthalpies of formation and standard entropies of $SrMoO_4$ nitridation reaction for Gibbs free energy calculation

	$SrMoO_4$	NH_3	$SrMoO_2N$	H_2O	H_2	N_2
Δ_fH (kJ/mol)	-1561.3*	-45.94	-1119.124*	-241.826	0	0
S^0 (J/mol▪K)[3]	128.9	192.776	107.417[a]	188.835	130.68	191.609

*: from our own calorimetric experiment results
[a]: estimated as the value of 5/6 $SrMoO_4$

Table S 10 The enthalpies of formation and standard entropies of $SrWO_4$ nitridation reaction for Gibbs free energy calculation

	$SrWO_4$	NH_3	$SrWO_{1.5}N_{1.5}$	H_2O	H_2	N_2
Δ_fH (kJ/mol)	-1641.2*	-45.94	-952.9*	-241.826	0	0
S^0 (J/mol▪K)[3, 4]	138.07	192.776	115.06[a]	188.835	130.68	191.609

*: from our own calorimetric experiment results
[a]: estimated as the value of 5/6 $SrWO_4$

References

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