Supporting Information

Metal Cation Effects on the Structural, Optical and Thermal Properties of the Double Tungstates $AM(WO_4)_2$ (A = Li, Na, K; M = Y, La, Ce, Pr, Nd, Sm, Bi)

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Crystal Data and Structure Refinements

Table S1. Crystal data and details of the structural refinements of selected double tungstates β-LiLa$(WO_4)_2$, α-LiPr$(WO_4)_2$, α -LiY$(WO_4)2$, and NaY$(WO_4)_2$ with single-crystal data reported for the first time, determined by single-crystal X-ray diffraction. Standard deviations are given in parentheses

	β-LiLa$(WO_4)_2$	α-LiPr$(WO_4)_2$	α-LiY$(WO_4)_2$	NaY$(WO_4)_2$
Temperature / K	298(2)	300(2)	300(2)	300(2)
Molar weight / g·mol^{-1}	641.55	643.55	599.55	607.60
Crystal system	Tetragonal	Triclinic	Monoclinic	Tetragonal
Space group	$I4_1/a$ (no. 88)	$P\bar{1}$ (no. 2)	$P2/n$ (no. 13)	$I4_1/a$ (no. 88)
a / Å	5.3352(3)	7.1028(1)	5.0038(1)	5.2090(2)
b / Å	5.3352(3)	7.3561(1)	5.7993(2)	5.2090(2)
c / Å	11.5736(8)	7.47920(1)	9.9959(3)	11.2930(5)
α / °	90	114.356(1)	90	90
β / °	90	115.555(1)	94.1853(3)	90
γ / °	90	91.063(1)	90	90
V / Å^3	329.44(4)	311.86(1)	289.29(1)	306.42(3)
Z	2	2	2	2
ρ / g·mol^{-1}	6.468	6.853	6.791	6.585
Absorption coefficient μ/ mm^{-1}	41.199	44.482	49.612	46.913
F(000)	544	548	508	524
Radiation; wavelength λ / Å	0.71073			
Diffractometer	Bruker D8 Venture			
θ range / °	4.206-29.724	3.131-32.494	3.513-27.976	4.309-32.404
Absorption correction	Multi-scan			
Transmission (min; max)	0.5423; 0.7490	0.4213; 0.7535	0.3308; 0.7503	0.6474; 0.7490
Index range $h\|k\|l$	-7/7|-7/7|-16/16	-10/10|-11/11|-11/11	-6/6|-7/7|-13/13	-7/7|-7/7|-16/16
Reflections collected	1957	37481	6256	2828
Independent reflections	242	2224	706	276
Obs. reflections	241	2097	693	243
Refined parameter	16	110	57	16
R_{int}	0.0281	0.0718	0.0339	0.0289
R_1 (all data)	0.0515	0.0362	0.0134	0.0170
wR_2	0.1262	0.0256	0.0313	0.0372
GooF	1.747	1.123	1.209	1.202
Residual electron density (max; min) / e$^-$Å^{-3}	2.946; -2.770	1.536; -0.912	1.958; -0.925	1.329; -0.920
CSD	2539263	2539264	2539265	2539266

Table S2. Crystal data and details of the structural refinements of selected double tungstates $NaBi(WO_4)_2$, $KLa(WO_4)_2$, $KY(WO_4)2$, and $KBi(WO_4)_2$ with single-crystal data reported for the first time, determined by single-crystal X-ray diffraction. Standard deviations are given in parentheses

	$NaBi(WO_4)_2$.	$KLa(WO_4)_2$	$KY(WO_4)_2$	$KBi(WO_4)_2$
Temperature / K	298(2)	300(2)	299(2)	300(2)
Molar weight / $g{\cdot}mol^{-1}$	727.67	673.71	623.71	743.78
Crystal system	Tetragonal	Tetragonal	Monoclinic	Monoclinic
Space group	$I4_1/a$ (no. 88)	$I4_1/a$ (no. 88)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a / Å	5.2823(9)	5.4442(2)	10.6245(4)	10.8170(4)
b / Å	5.2823(9)	5.4442(2)	10.3366(4)	10.5611(4)
c / Å	11.509(2)	12.1406(6)	7.5497(3)	7.6045(3)
α / °	90	90	90	90
β / °	90	90	130.7421(9)	130.8497(7)
γ / °	90	90	90	90
V / $Å^3$	321.12(12)	359.84(3)	628.18	657.13(4)
Z	2	2	4	4
ρ / $g{\cdot}mol^{-1}$	7.526	6.218	6.595	7.518
Absorption coefficient μ/ mm^{-1}	63.139	38.300	46.362	62.276
F(000)	612	576	1080	1256
Radiation; wavelength λ / Å	0.71073			
Diffractometer	Bruker D8 Venture			
θ range / °	4.245-35.978	4.102-32.962	3.208-34.962	3.149-34.999
Absorption correction	Multi-scan			
Transmission (min; max)	0.4861; 0.7490	0.4672; 0.7516	0.6156; 0.7490	0.5701; 0.7479
Index range $h\|k\|l$	-8/7|-8/8|-18/18	-8/8|-8/8|-18/18	17/17|-16/16|-12/12	17/17|-16/16|-12/12
Reflections collected	2286	47796	9999	12151
Independent reflections	383	338	1387	1450
Obs. reflections	320	335	1151	1301
Refined parameter / restraints	16	16	57	57
R_{int}	0.0317	0.0498	0.0368	0.0412
R_1 (all data)	0.0262	0.0290	0.0295	0.0240
wR_2	0.0355	0.0659	0.0386	0.0320
GooF	1.044	1.491	1.054	1.068
Residual electron density (max; min) / $e{\cdot}Å^{-3}$	1.552; -0.888	1.190; -1.499	1.753; -1.426	1.835; -1.625
CSD	2539270	2539267	2539268	2539269

Table S3. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å² in α-LiLa$(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
W1	2i	0.25697(2)	0.79481(2)	0.52450(2)	0.00528(4)
W2	2i	0.35611(2)	0.39794(2)	0.21691(2)	0.00520(4)
La1	2i	0.81698(3)	0.21577(3)	0.04478(3)	0.00602(4)
Li1	2i	-0.2593(14)	0.8194(14)	0.4846(17)	0.0280(19)
O1	2i	0.2975(5)	0.4858(4)	0.0203(5)	0.0124(5)
O2	2i	0.1820(4)	0.8650(4)	0.3083(4)	0.0103(5)
O3	2i	0.0385(4)	0.8013(4)	0.5822(4)	0.0097(5)
O4	2i	0.4394(4)	1.0335(4)	0.7473(4)	0.0116(5)
O5	2i	0.1815(4)	0.1459(4)	0.0678(4)	0.0094(5)
O6	2i	0.6158(4)	0.3317(4)	0.2467(4)	0.0087(5)
O7	2i	0.1396(4)	0.4921(4)	0.3025(4)	0.0081(4)
O8	2i	0.5159(4)	0.6730(4)	0.4896(4)	0.0067(4)

Table S4. Anisotropic displacement parameters U_{ij} / Å² in α-LiLa$(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
W1	0.00576(6)	0.00522(6)	0.00553(6)	0.00188(4)	0.00306(5)	0.00267(5)
W2	0.00485(6)	0.00481(6)	0.00566(6)	0.00133(4)	0.00228(5)	0.00245(5)
La1	0.00585(8)	0.00607(8)	0.00599(8)	0.00132(6)	0.00294(6)	0.00258(6)
Li1	0.018(4)	0.028(4)	0.052(6)	0.011(3)	0.023(4)	0.024(4)
O1	0.0153(13)	0.0131(13)	0.0138(12)	0.0067(10)	0.0080(11)	0.0093(11)
O2	0.0137(12)	0.0111(12)	0.0086(11)	0.0049(10)	0.006(1)	0.006(1)
O3	0.0065(11)	0.0105(12)	0.0120(11)	0.0023(9)	0.0048(9)	0.0047(10)
O4	0.0089(12)	0.0087(12)	0.0120(12)	0.0002(9)	0.0037(10)	0.0018(10)
O5	0.0076(11)	0.0066(11)	0.0119(12)	0.0017(9)	0.0035(10)	0.0038(9)
O6	0.0086(11)	0.0130(12)	0.0101(11)	0.0052(9)	0.0061(9)	0.0082(10)
O7	0.0063(11)	0.0066(11)	0.0088(11)	0.0015(9)	0.0029(9)	0.0019(9)
O8	0.0059(11)	0.0069(11)	0.0074(10)	0.0018(9)	0.0037(9)	0.0027(9)

Table S5. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å² in α-LiPr$(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
W1	2i	0.25833(2)	0.79567(2)	0.52636(2)	0.00504(3)
W2	2i	0.35458(2)	0.39597(2)	0.21270(2)	0.00493(3)
Pr1	2i	0.81880(2)	0.21613(2)	0.04482(2)	0.00571(3)
Li1	2i	-0.2613(11)	0.8187(11)	0.4818(15)	0.0257(14)
O1	2i	0.2940(4)	0.4851(3)	0.0151(4)	0.0112(3)
O2	2i	0.1818(4)	0.8639(3)	0.3066(3)	0.0102(3)
O3	2i	0.0397(3)	0.8028(3)	0.5870(4)	0.0099(3)
O4	2i	0.4442(3)	1.0369(3)	0.7512(3)	0.0112(3)
O5	2i	0.1799(3)	0.1416(3)	0.0630(3)	0.0095(3)
O6	2i	0.6162(3)	0.3302(3)	0.2429(3)	0.0078(3)
O7	2i	0.1372(3)	0.4899(3)	0.3010(3)	0.0078(3)

O8	2i	0.5156(3)	0.6730(3)	0.4889(3)	0.0061(3)

Table S6. Anisotropic displacement parameters U_{ij} / Å² in α-LiPr$(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
W1	0.00519(5)	0.00507(4)	0.00543(4)	0.00170(3)	0.00287(3)	0.00259(3)
W2	0.00436(4)	0.00468(4)	0.00543(4)	0.00113(3)	0.00211(3)	0.00235(3)
Pr1	0.00527(6)	0.00583(5)	0.00578(5)	0.00100(4)	0.00265(4)	0.00252(4)
Li1	0.016(3)	0.026(3)	0.049(4)	0.009(2)	0.019(3)	0.025(3)
O1	0.0128(9)	0.0126(8)	0.0119(8)	0.0049(7)	0.0065(7)	0.0082(7)
O2	0.0122(9)	0.0115(8)	0.0082(7)	0.0040(7)	0.0046(7)	0.0061(7)
O3	0.0095(8)	0.0120(8)	0.0120(8)	0.0051(7)	0.0069(7)	0.0069(7)
O4	0.0086(8)	0.0089(8)	0.0108(8)	0.0003(6)	0.0036(7)	0.0014(7)
O5	0.0074(8)	0.0060(7)	0.0112(8)	0.0005(6)	0.0025(7)	0.0028(6)
O6	0.0081(8)	0.0115(8)	0.0084(7)	0.0052(6)	0.0061(6)	0.0064(6)
O7	0.0046(7)	0.0079(7)	0.0093(7)	0.0010(6)	0.0038(6)	0.0024(6)
O8	0.0047(7)	0.0064(7)	0.0081(7)	0.0013(6)	0.0034(6)	0.0039(6)

Table S7. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å² in α-LiY$(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
Y1	2f	5/4	0.70064(9)	-1/4	0.00909(12)
Li1	2e	5/4	-0.261(3)	1/4	0.027(2)
W1	4g	0.75229(2)	0.81859(2)	0.01698(2)	0.00634(9)
O1	4g	0.9087(5)	0.6259(5)	0.1360(3)	0.0094(5)
O2	4g	1.0482(5)	0.8919(5)	-0.0953(2)	0.0093(5)
O3	4g	0.6057(6)	0.6270(5)	-0.1067(3)	0.0123(5)
O4	4g	0.4730(5)	0.9183(5)	0.1148(3)	0.0127(5)

Table S8. Anisotropic displacement parameters U_{ij} / Å² in α-LiY$(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Y1	0.0126(2)	0.0100(2)	0.0050(2)	0.00000	0.00243(19)	0.00000
Li1	0.017(5)	0.045(7)	0.020(6)	0.00000	-0.002(4)	0.00000
W1	0.00658(11)	0.00748(11)	0.00504(11)	0.00036(4)	0.00103(6)	0.00073(4)
O1	0.0108(12)	0.0092(11)	0.0081(12)	0.0003(11)	0.001(1)	0.0004(10)
O2	0.0126(12)	0.0081(12)	0.0077(11)	-0.0002(10)	0.0031(9)	-0.0002(9)
O3	0.0138(13)	0.0142(13)	0.0086(12)	-0.0024(11)	-0.0003(10)	0.0007(11)
O4	0.0127(12)	0.0171(14)	0.0088(11)	0.0044(11)	0.0047(10)	0.0044(10)

Table S9. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å² in β-LiLa$(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
La1	4a	0.54(2)	0	1/4	1/8	0.0138(18)
Li1	4a	0.46(2)	0	1/4	1/8	0.0138(18)
W1	4b		01. Feb	1/4	1/8	0.0112(8)

O1	16f	0.262(3)	0.603(3)	0.0404(12)	0.0404(12)

Table S10. Anisotropic displacement parameters U_{ij} / Å^2 in β-LiLa$(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
La1	0.0131(19)	0.0131(19)	0.015(2)	0.00000	0.00000	0.00000
Li1	0.0131(19)	0.0131(19)	0.015(2)	0.00000	0.00000	0.00000
W1	0.0095(8)	0.0095(8)	0.0145(10)	0.00000	0.00000	0.00000
O1	0.015(6)	0.005(6)	0.017(6)	-0.003(5)	-0.004(5)	0.002(5)

Table S11. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in β-LiPr$(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Pr1	4a	0.511(5)	0	1/4	1/8	0.0112(4)
Li1	4a	0.489(5)	0	1/4	1/8	0.0112(4)
W1	4b		1/2	3/4	1/8	0.01400(18)
O1	16f		0.2604(8)	0.5992(7)	0.0400(4	0.0182(7)

Table S12. Anisotropic displacement parameters U_{ij} / Å^2 in β-LiPr$(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Pr1	0.0115(4)	0.0115(4)	0.0104(5)	0.00000	0.00000	0.00000
Li1	0.0115(4)	0.0115(4)	0.0104(5)	0.00000	0.00000	0.00000
W1	0.01124(19)	0.01124(19)	0.0195(2)	0.00000	0.00000	0.00000
O1	0.0201(17)	0.0146(15)	0.0199(15)	-0.0030(13)	-0.0046(13)	0.0010(13)

Table S13. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in β-LiY$(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F	*x*	*y*	*z*	U_{eq}
Y1	4a	0.481(8)	0	1/4	1/8	0.0081(7)
Li1	4a	0.519(8)	0	1/4	1/8	0.0081(7)
W1	4b		1/2	3/4	1/8	0.01421(16)
O1	16f		0.6597(10)	0.5051(10)	0.2108(5)	0.2108(5)

Table S14. Anisotropic displacement parameters U_{ij} / Å^2 in β-LiY$(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Y1	0.0089(8)	0.0089(8)	0.0065(10)	0.00000	0.00000	0.00000
Li1	0.0089(8)	0.0089(8)	0.0065(10)	0.00000	0.00000	0.00000
W1	0.01294(18)	0.01294(18)	0.0167(3)	0.00000	0.00000	0.00000
O1	0.018(2)	0.024(3)	0.019(2)	0.0042(19)	-0.0008(19)	0.005(2)

Table S15. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å² in $LiBi(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
Li1	2e	-1/4	-0.253(4)	3/4	0.031(4)
Bi1	2f	1/4	0.31915(4)	3/4	0.00891(10)
W1	4g	0.24923(4)	-0.17340(3)	0.51695(2)	0.00628(9)
O1	4g	0.0881(8)	0.6473(6)	0.8660(4)	0.0120(7)
O2	4g	0.0560(7)	0.1008(6)	0.9029(3)	0.0098(6)
O3	4g	0.1222(8)	-0.3626(7)	0.3938(4)	0.0145(7)
O4	4g	-0.0470(7)	-0.0898(7)	0.6088(3)	0.0116(7)

Table S16. Anisotropic displacement parameters U_{ij} / Å² in $LiBi(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Li1	0.024(8)	0.047(11)	0.024(8)	0.00000	0.021(7)	0.00000
Bi1	0.01219(16)	0.00741(15)	0.00712(13)	0.00000	0.00009(9)	0.00000
W1	0.00599(13)	0.00653(13)	0.00629(12)	0.00030(6)	-0.00039(7)	0.00063(6)
O1	0.0116(17)	0.0106(17)	0.0136(16)	0.0003(13)	-0.0014(13)	-0.0011(13)
O2	0.0094(16)	0.0103(16)	0.0098(14)	0.0017(13)	0.0028(12)	0.0029(12)
O3	0.0152(18)	0.0128(17)	0.0151(16)	0.0008(14)	-0.0032(14)	-0.0013(14)
O4	0.0098(16)	0.0166(18)	0.0085(14)	0.0036(14)	0.0016(12)	0.0049(13)

Table S17. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å² in $NaY(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Y1	4b	0.455(11)	1/2	3/4	1/8	0.0059(6)
Na1	4b	0.545(11)	1/2	3/4	1/8	0.0059(6)
O1	16f		0.2426(6)	0.4062(5)	0.0393(3)	0.0393(3)
W1	4a		0	1/4	1/8	0.00888(17)

Table S18. Anisotropic displacement parameters U_{ij} / Å² in $NaY(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Y1	0.0059(6)	0.0059(6)	0.0058(7)	0.00000	0.00000	0.00000
Na1	0.0059(6)	0.0059(6)	0.0058(7)	0.00000	0.00000	0.00000
O1	0.0211(13)	0.0138(12)	0.0165(11)	-0.0031(10)	0.0057(10)	0.0008(10)
W1	0.00758(17)	0.00758(17)	0.0115(2)	0.00000	0.00000	0.00000

Table S19. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å² in $NaBi(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
Na1	4b	0.496(2)	1/2	3/4	1/8	0.0147(2)
Bi1	4b	0.504(2)	1/2	3/4	1/8	0.0147(2)

W1	4a	0	1/4	1/8	0.01074(11)
O1	16f	1.3480(5)	0.4891(5)	0.2909(2)	0.0185(5)

Table S20. Anisotropic displacement parameters U_{ij} / Å^2 in $NaBi(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Na1	0.0127(2)	0.0127(2)	0.0188(2)	0.00000	0.00000	0.00000
Bi1	0.0127(2)	0.0127(2)	0.0188(2)	0.00000	0.00000	0.00000
W1	0.00908(12)	0.00908(12)	0.01406(14)	0.00000	0.00000	0.00000
O1	0.0143(12)	0.0235(13)	0.0178(10)	0.0032(9)	0.0012(9)	0.0055(9)

Table S21. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $KLa(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	S.O.F.	*x*	*y*	*z*	U_{eq}
K1	4a	0.541(10)	0	1/4	1/8	0.0062(5)
La1	4a	0.459(10)	0	1/4	1/8	0.0062(5)
W1	4b		1/2	3/4	1/8	0.0111(3)
O1	16f		0.2625(13)	0.6142(12)	0.0452(6)	0.0249(13)

Table S22. Anisotropic displacement parameters U_{ij} / Å^2 in $KLa(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
K1	0.0071(5)	0.0071(5)	0.0046(6)	0.00000	0.00000	0.00000
La1	0.0071(5)	0.0071(5)	0.0046(6)	0.00000	0.00000	0.00000
W1	0.0094(3)	0.0094(3)	0.0146(3)	0.00000	0.00000	0.00000
O1	0.032(3)	0.015(2)	0.027(3)	-0.004(2)	-0.015(3)	-0.003(2)

Table S23. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $KY(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
W1	8f	0.19614(2)	0.00015(2)	0.23585(2)	0.00478(5)
Y1	4e	0	-0.27157(5)	1/4	0.00547(9)
K1	4e	0	0.30036(13)	1/4	0.0153(2)
O1	8f	0.0236(3)	0.1082(3)	-0.0307(5)	0.0071(5)
O2	8f	0.2754(3)	-0.1581(2)	0.3749(5)	0.0085(5)
O4	8f	0.3741(3)	0.0803(3)	0.3116(5)	0.0085(5)
O3	8f	0.1901(3)	0.0759(3)	0.4417(5)	0.0084(5)

Table S24. Anisotropic displacement parameters U_{ij} / Å^2 in $KY(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
W1	0.00451(6)	0.00455(7)	0.00456(6)	-0.00014(5)	0.00264(5)	0.00058(5)
Y1	0.0069(2)	0.00402(18)	0.0055(2)	0.00000	0.00406(18)	0.00000
K1	0.0146(6)	0.0145(6)	0.0147(6)	0.00000	0.0086(5)	0.00000
O1	0.0055(11)	0.0059(11)	0.0081(12)	0.0000(8)	0.0037(10)	0.0014(9)

O2	0.0096(12)	0.0071(11)	0.0057(12)	0.0011(9)	0.0037(10)	0.0016(9)
O4	0.0084(12)	0.0098(12)	0.0079(12)	-0.0005(10)	0.0056(11)	0.0018(10)
O3	0.0086(12)	0.0083(12)	0.0090(12)	-0.0017(9)	0.0062(11)	0.0009(9)

Table S25. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters U_{eq} / Å^2 in $KBi(WO_4)_2$. Standard deviations are given in parentheses

Atom	Wyckoff symbol	*x*	*y*	*z*	U_{eq}
Bi1	4e	0	0.27356(2)	1/4	0.00974(5)
W1	8f	0.19434(2)	0.00020(2)	0.23411(2)	0.00612(4)
K1	4e	0	0.29746(13)	-1/4	0.0195(3)
O1	8f	0.3114(3)	0.5696(2)	0.5589(5)	0.0113(5)
O2	8f	0.0229(3)	-0.1067(2)	-0.0254(4)	0.0086(5)
O3	8f	0.2726(3)	0.1569(2)	0.3648(5)	0.0129(5)
O4	8f	0.3702(3)	-0.0790(3)	0.3142(5)	0.0132(5)

Table S26. Anisotropic displacement parameters U_{ij} / Å^2 in $KBi(WO_4)_2$. Standard deviations are given in parentheses

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Bi1	0.01371(9)	0.00718(8)	0.01020(9)	0.00000	0.00864(7)	0.00000
W1	0.00647(6)	0.00572(6)	0.00584(6)	0.00023(4)	0.00387(5)	-0.00072(4)
K1	0.0195(6)	0.0189(6)	0.0179(6)	0.00000	0.0112(5)	0.00000
O1	0.0134(12)	0.0113(12)	0.0115(12)	-0.0001(9)	0.0091(10)	0.0008(9)
O2	0.0088(11)	0.0079(11)	0.0087(12)	0.0008(8)	0.0055(10)	-0.0011(9)
O3	0.0131(12)	0.0091(12)	0.0101(13)	-0.0011(9)	0.0048(11)	-0.0027(9)
O4	0.0113(12)	0.0157(13)	0.0131(13)	0.0030(9)	0.0082(11)	-0.0011(10)

Powder X-ray Diffraction Patterns

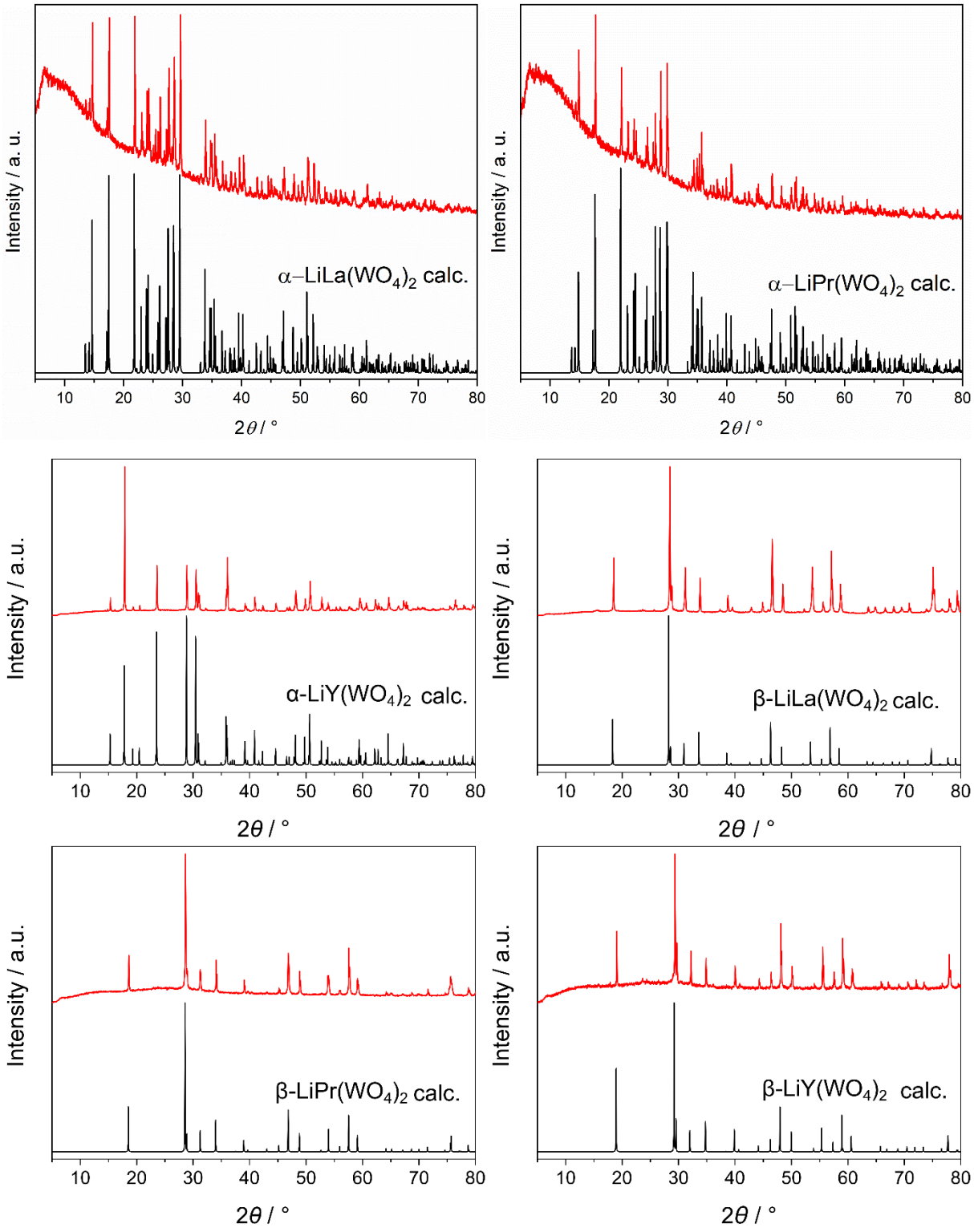

Figure S1. Powder diffraction data of respective double tungstates compared to the calculated patterns out of single crystal X-ray diffraction measurements.

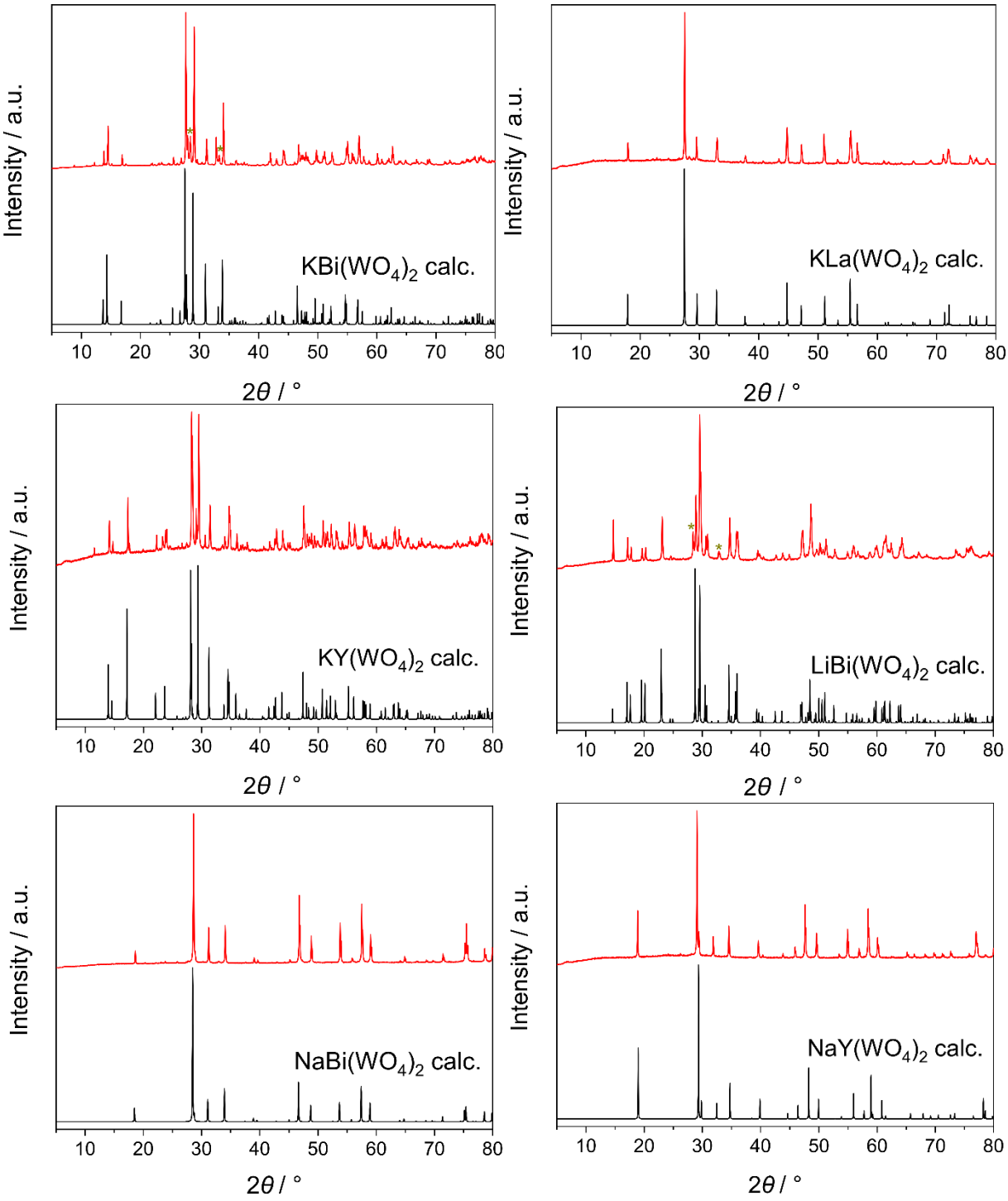

Figure S2. Powder diffraction data of respective double tungstates compared to the calculated patterns out of single crystal X-ray diffraction measurements.

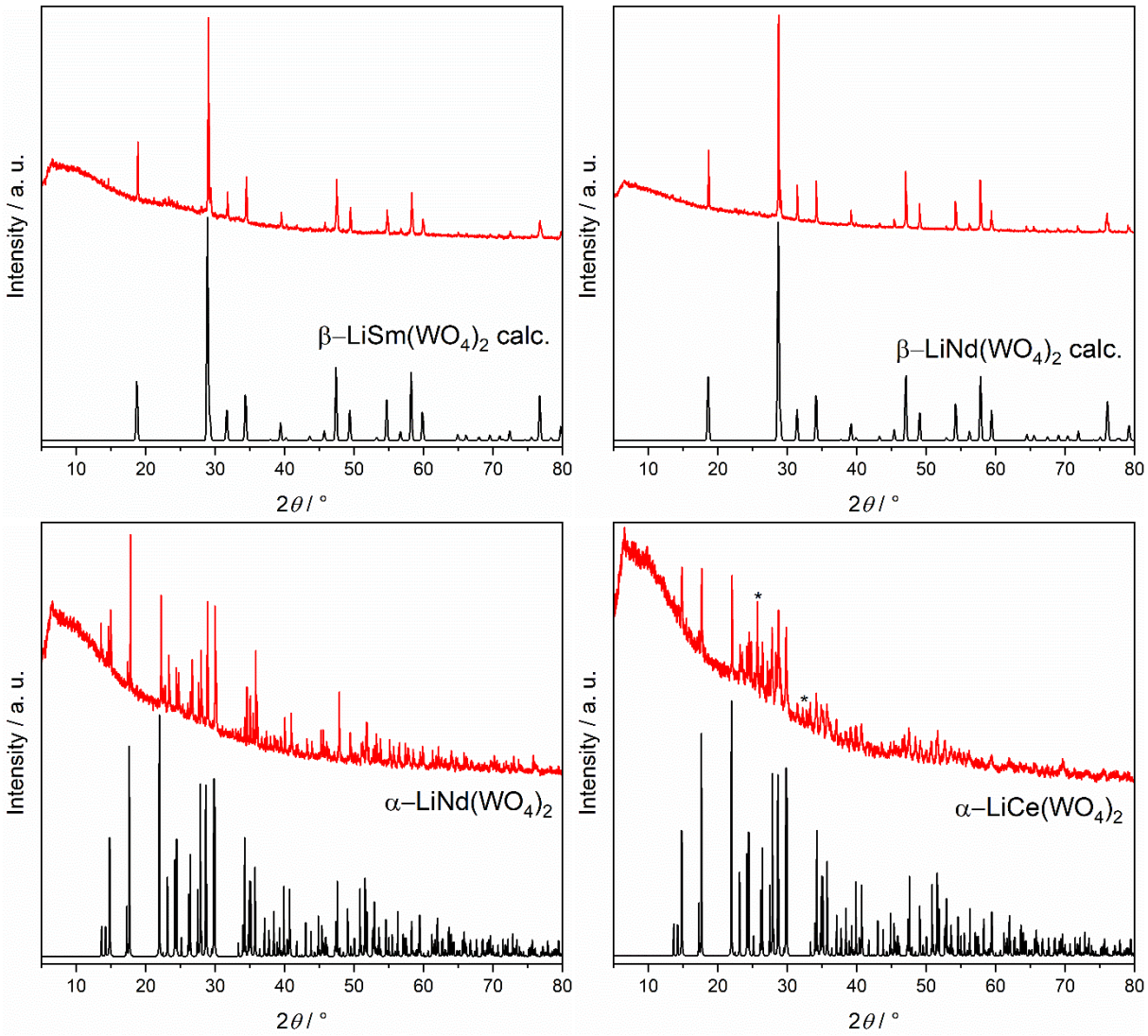

Figure S3. Powder diffraction data of respective double tungstates compared to the calculated patterns out of single crystal X-ray diffraction measurements.

UV-Vis and Photoluminescence Spectra

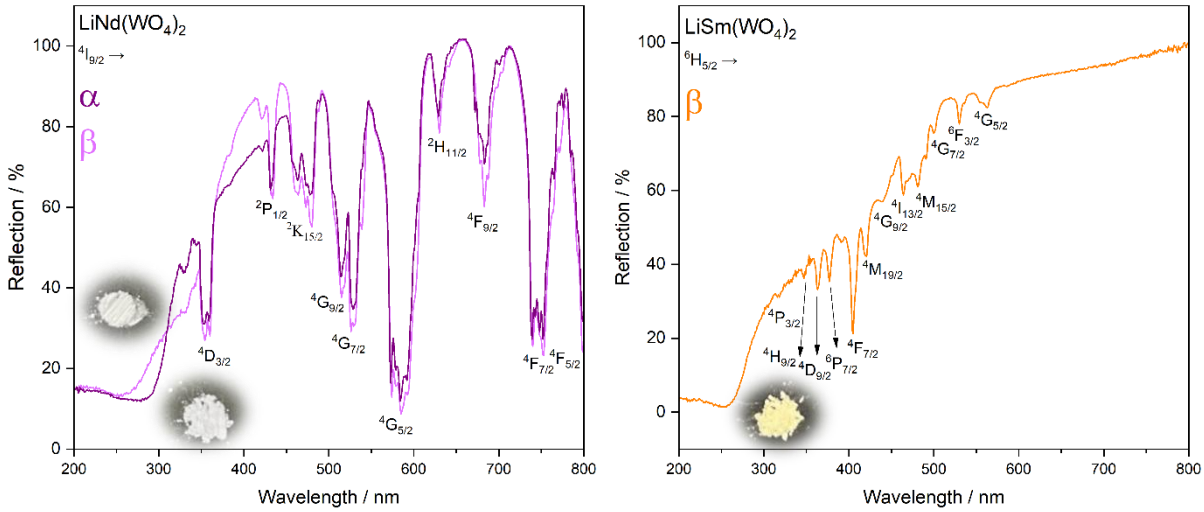

Figure S4. UV-vis spectra of respective double tungstates $LiNd(WO_4)_2$ and β-$LiSm(WO_4)_2$.

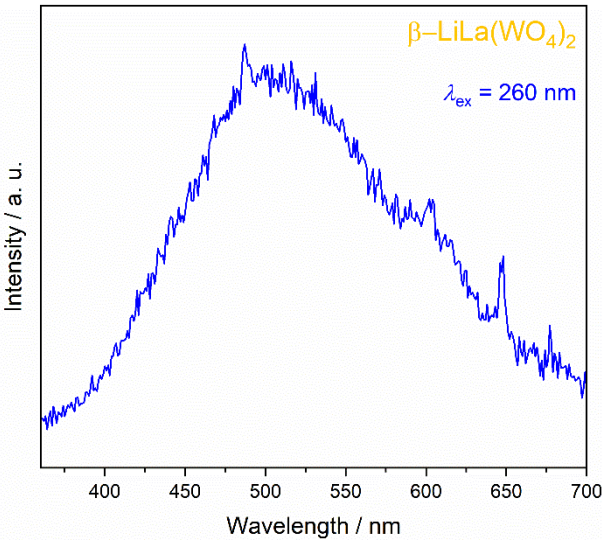

Figure S5. Emission spectrum of β-$LiLa(WO_4)_2$.

Thermal Analysis

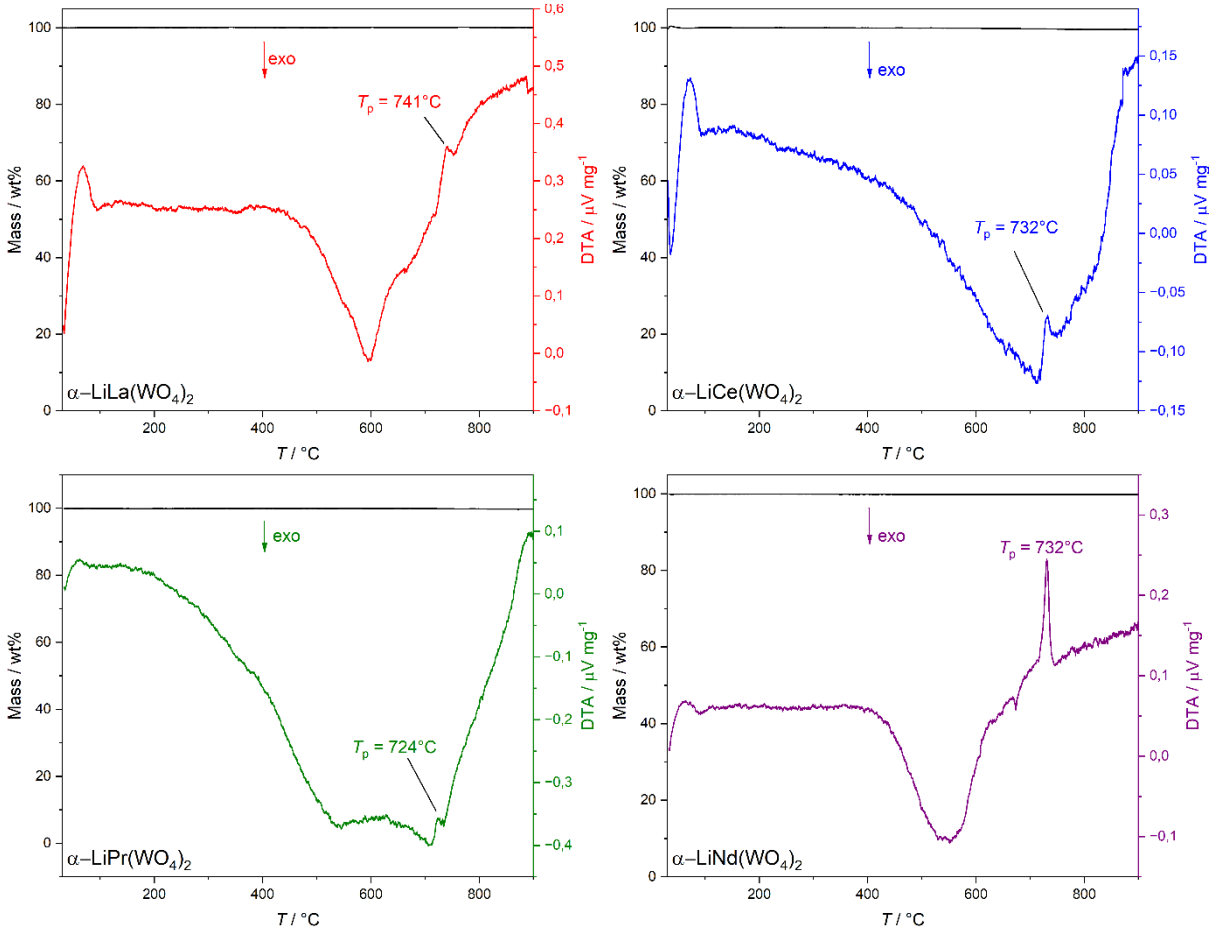

Figure S6. Thermogravimetric measurements of the low-temperature phases α-LiM$(WO_4)_2$.

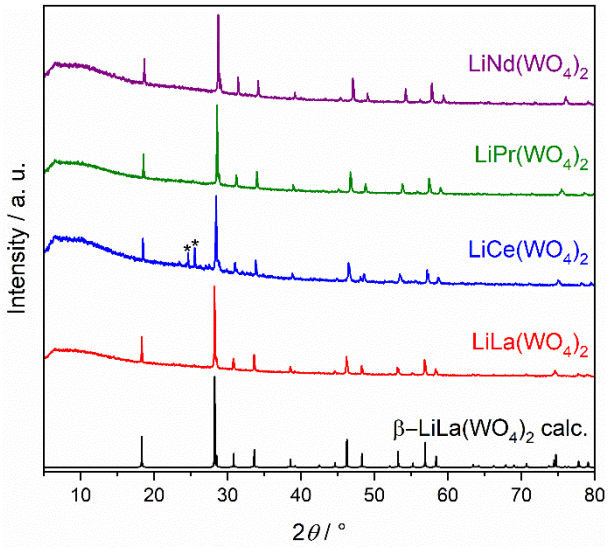

Figure S7. Powder diffraction measurements after thermogravimetric analysis of α-LiM$(WO_4)_2$.

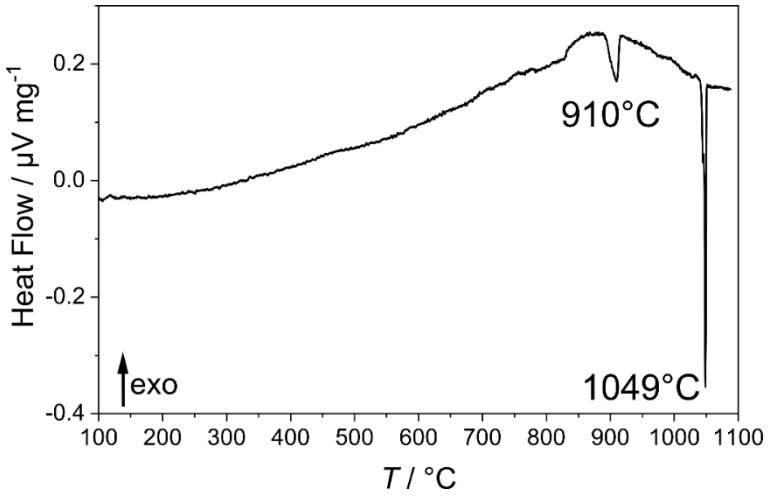

Figure S8. Differential Scanning Calorimetry measurement of α-LiY$(WO_4)_2$.

Selected Ionic Radii after Shannon

Table S27. Ionic radii / pm after Shannon[1] with respect to their coordination number

Ion	Charge	Coordination	Ionic radius / pm
Li	1	IV	59
Li	1	VIII	92
Na	1	VIII	118
K	1	VIII	151
K	1	X	159
La	3	VIII	116
Bi	3	VIII	117
W	6	IV	42
W	6	VI	60
O	-2	II	135
O	-2	III	136
O	-2	IV	138

Table S28. Ratio of the cationic radii A = Li, Na, K and M = Bi, La, Ce, Pr, Nd, Sm, Y in the double tungstates. The radii were adjusted to the respective coordination number of the structure types

$^{A}/_{M}$	Bi^{3+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Y^{3+}
Li^{+} α-phase	-	0.51	0.52	0.52	0.53	0.55	0.58
Li^{+} β-phase	0.50	0.79	0.80	0.82	0.83	0.85	0.90
Na^{+}	1.01	1.02	1.03	1.05	1.06	1.09	1.16
K^{+}	1.36	1.30	1.32	1.34	1.36	1.47	1.56

MAPLE Calculations

Table S29. Calculated MAPLE values of the binary and tertiary compounds

Compound	MAPLE Value in kJ mol^{-1}
Li_2O	3506[2]
Li_2WO_4	28712[3]
Na_2O	2907[4]
K_2O	2511[5]
La_2O_3	9397[6]
Pr_2O_3	14418[7]
Y_2O_3	15270[8]
Bi_2O_3	14380[9]
WO_3	25945[10]

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