# Supplementary Information

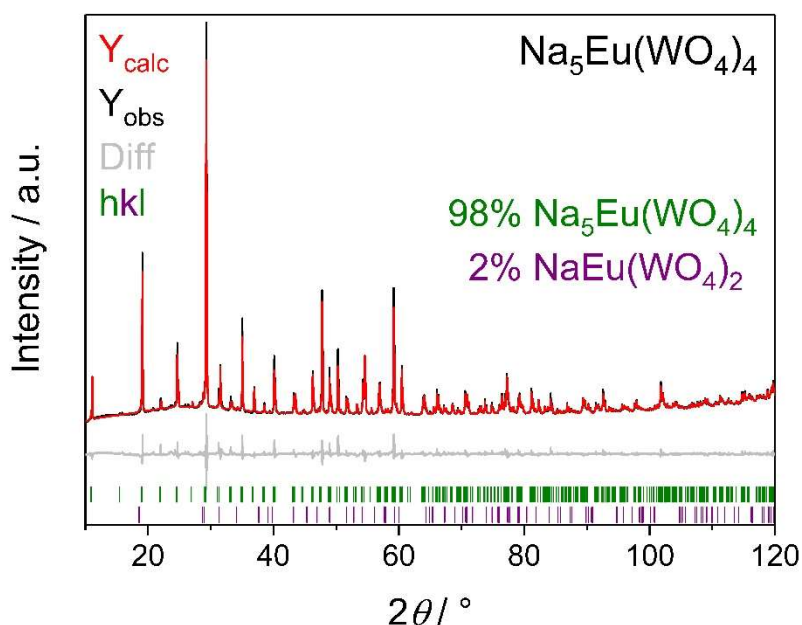

**Fig. S1: Rietveld-Refinement of Na₅Eu(WO₄)₄ prepared by flux synthesis; further details can be found in Table S3.**



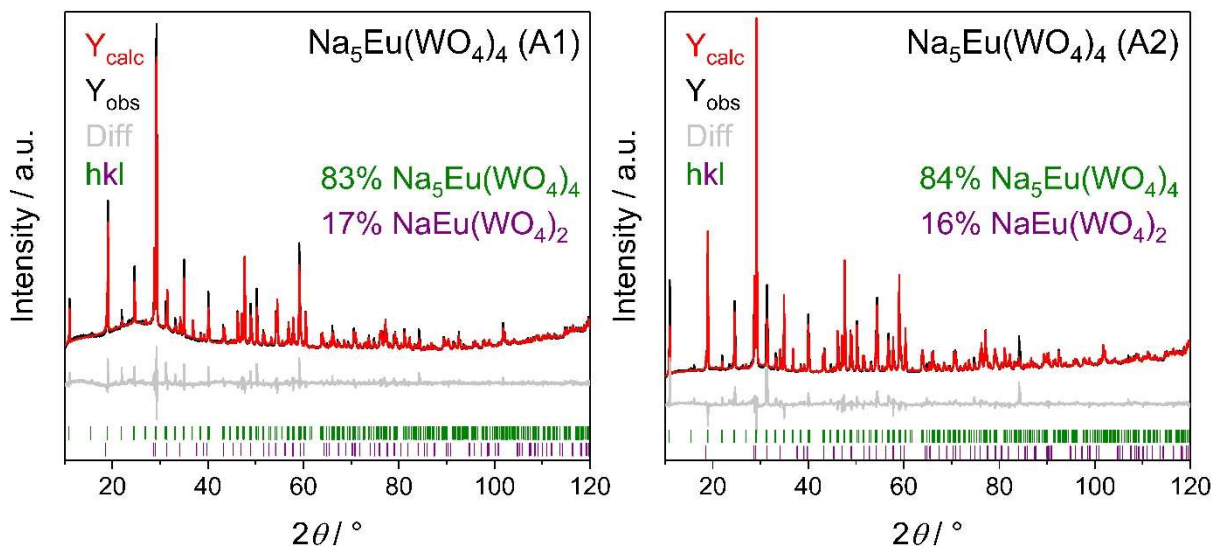**Fig. S2: Rietveld refinements of Na₅Eu(WO₄)₄ prepared by standard solid state reaction at 600°C (A1) (left) and 700°C (A2) (right): the refinements yielded in $R_{wp}$ of 2.24% and 4.23%, $R_{Bragg}$ of 1.29% and 2.91% for Na₅Eu(WO₄)₄ and 0.72% and 1.77% for NaEu(WO₄)₂, respectively.**

**Table S1.** Crystal data and structure refinements of $NaEu(WO_4)_2$ and $Na_5M(WO_4)_4$ (M = Ce, Pr, Nd, Sm, Eu) determined from single-crystal data[a]

| | $NaEu(WO_4)_2$ | $Na_5Ce(WO_4)_4$ | $Na_5Pr(WO_4)_4$ | $Na_5Nd(WO_4)_4$ | $Na_5Sm(WO_4)_4$ | $Na_5Eu(WO_4)_4$ |
|---|---|---|---|---|---|---|
| CSD-No. | 1986866 | 1986870 | 1986859 | 1986871 | 1986862 | 1986865 |
| $M$ / g mol$^{-1}$ | 670.65 | 1246.47 | 1247.26 | 1250.59 | 1256.70 | 1258.31 |
| Crystal size / mm$^3$ | 0.04 × 0.04 × 0.03 | 0.07 × 0.03 × 0.03 | 0.04 × 0.04 × 0.04 | 0.04 × 0.04 × 0.03 | 0.04 × 0.04 × 0.02 | 0.10 × 0.06 × 0.03 |
| Temperature / K | 300(3) | | | | | |
| Space group | $I4_1/a$ (No. 88) | | | | | |
| $a$ / pm | 526.24(1) | 1158.57(3) | 1157.65(2) | 1155.89(4) | 1151.61(4) | 1149.98(4) |
| $c$ / pm | 1140.78(3) | 1152.47(4) | 1147.97(2) | 1147.22(4) | 1142.31(4) | 1140.61(4) |
| Volume / $10^6$ pm$^3$ | 316.07(3) | 1546.94(10) | 1538.46(6) | 1532.78(12) | 1514.94(12) | 1508.40(12) |
| $Z$ | 2 | 4 | | | | |
| $\rho_{calcd}$ / g cm$^{-3}$ | 7.05 | 5.35 | 5.39 | 5.42 | 5.51 | 5.54 |
| Absorption coefficient $\mu$ / mm$^{-1}$ | 46.2 | 32.7 | 33.1 | 33.5 | 34.3 | 34.7 |
| $F(000)$ / $e$ | 572 | 2148 | 2152 | 2156 | 2164 | 2168 |
| Radiation; wavelength $\lambda$ / Å | Mo$K\alpha$; 0.71073 | | | | | |
| Diffractometer | Bruker D8 Venture | | | | | |
| Absorption correction | Multi-scan | | | | | |
| Transmission (min; max) | 0.6338; 0.7503 | 0.6678; 0.7478 | 0.6011; 0.7488 | 0.5281; 0.7472 | 0.5921; 0.7479 | 0.6001; 0.7483 |
| Index range $h$\|$k$\|$l$ | −9/9\|−9/9\|−21/21 | −14/16\|−15/16\|−15/15 | −19/21\|−21/21\|−20/20 | −17/16\|−16/17\|−17/17 | −18/19\|−19/19\|−19/19 | −20/20\|−15/20\|−20/20 |
| $\theta$ range / deg | 4.265–41.863 | 2.493–29.415 | 2.499–40.487 | 2.501–33.497 | 2.511–36.979 | 2.515–39.996 |
| Reflections collected | 21433 | 9235 | 26586 | 13470 | 18168 | 16901 |
| Independent reflections | 546 | 1062 | 2455 | 1504 | 1937 | 2337 |
| $R_{int}$ | 0.0284 | 0.0325 | 0.0504 | 0.056 | 0.0403 | 0.0406 |
| Obs. reflections ($I > 2\,\sigma(I)$) | 472 | 1008 | 2191 | 1277 | 1722 | 2025 |
| Refined parameters | 16 | 59 | 60 | 60 | 60 | 60 |
| $R_1$ (all data) | 0.018 | 0.0321 | 0.024 | 0.0322 | 0.023 | 0.0258 |
| $wR_2$ (all data) | 0.034 | 0.0719 | 0.0298 | 0.0362 | 0.0321 | 0.0356 |
| GooF | 1.12 | 1.342 | 1.076 | 1.038 | 1.038 | 1.026 |
| Residual electron density (max; min) / $e^-$ Å$^{-3}$ | 2.08; −1.51 | 2.16; −2.13 | 1.16; −1.22 | 1.08; −1.18 | 1.56; −1.10 | 1.41; −1.18 |

[a] The respective standard deviations are given in parentheses.

**Table S2.** Crystal data and structure refinements of $Na_5M(WO_4)_4$ (M = Gd, Tb, Ho, Tm, Yb, Bi) determined from single-crystal data[a]

| | $Na_5Gd(WO_4)_4$ | $Na_5Tb(WO_4)_4$ | $Na_5Ho(WO_4)_4$ | $Na_5Tm(WO_4)_4$ | $Na_5Yb(WO_4)_4$ | $Na_5Bi(WO_4)_4$ |
|---|---|---|---|---|---|---|
| CSD-No. | 1986868 | 1986861 | 1986869 | 1986863 | 1986867 | 1986858 |
| $M$ / g mol$^{-1}$ | 1263.60 | 1265.27 | 1271.28 | 1275.28 | 1279.39 | 1315.33 |
| Crystal size / mm$^3$ | 0.06 × 0.04 × 0.04 | 0.08 × 0.04 × 0.03 | 0.06 × 0.06 × 0.04 | 0.08 × 0.05 × 0.04 | 0.05 × 0.05 × 0.04 | 0.08 × 0.04 × 0.03 |
| Temperature / K | | | 300(3) | | | |
| Space group | | | $I4_1/a$ (No. 88) | | | |
| $a$ / pm | 1147.96(4) | 1146.90(5) | 1143.99(4) | 1139.99(6) | 1139.65(10) | 1154.33(4) |
| $c$ / pm | 1137.79(4) | 1137.91(6) | 1134.69(5) | 1129.85(6) | 1129.32(11) | 1141.36(4) |
| Volume / $10^6$ pm$^3$ | 1499.39(12) | 1496.78(15) | 1484.98(12) | 1468.33(17) | 1466.8(3) | 1520.84(12) |
| Z | | | 4 | | | |
| $\rho_{calcd}$ / g cm$^{-3}$ | 5.60 | 5.61 | 5.69 | 5.77 | 5.79 | 5.75 |
| Absorption coefficient $\mu$ / mm$^{-1}$ | 35.2 | 35.5 | 36.4 | 37.4 | 37.8 | 41.9 |
| $F(000)$ / $e$ | 2172 | 2176 | 2184 | 2192 | 2196 | 2248 |
| Radiation; wavelength $\lambda$ / Å | | | $MoK\alpha$; 0.71073 | | | |
| Diffractometer | | | Bruker D8 Venture | | | |
| Absorption correction | | | Multi-scan | | | |
| Transmission (min; max) | 0.5701; 0.7492 | 0.5804; 0.7479 | 0.4945; 0.7489 | 0.5591; 0.7506 | 0.4954; 0.7477 | 0.6549; 0.7459 |
| Index range $h\|k\|l$ | −20/16\|−20/20\|− | −19/19\|−19/14\|−19/19 | −19/19\|−19/13\|−19/19 | −20/20\|−20/18\|−20/20 | −12/19\|−18/19\|−18/18 | −15/15\|−15/15\|−15/15 |
| $\theta$ range / deg | 2.520–40.496 | 2.521–37.475 | 2.528–37.999 | 2.538–39.496 | 2.539–36.400 | 2.510– 29.246 |
| Reflections collected | 23034 | 15674 | 15782 | 18502 | 13271 | 12840 |
| Independent reflections | 2397 | 1961 | 2021 | 2215 | 1795 | 1040 |
| $R_{int}$ | 0.0459 | 0.044 | 0.0378 | 0.0449 | 0.0468 | 0.0521 |
| Obs. reflections ($I > 2\,\sigma(I)$) | 2116 | 1718 | 1795 | 1940 | 1533 | 912 |
| Refined parameters | 60 | 60 | 60 | 60 | 60 | 60 |
| $R_1$ (all data) | 0.0243 | 0.0282 | 0.0252 | 0.0266 | 0.03 | 0.025 |
| $wR_2$ (all data) | 0.0349 | 0.04 | 0.0354 | 0.0363 | 0.0391 | 0.0307 |
| GooF | 1.081 | 1.095 | 1.086 | 1.076 | 1.049 | 1.069 |
| Residual electron density (max; min) / $e^-$ Å$^{-3}$ | 2.05; -1.12 | 1.99; −1.21 | 1.45; −1.19 | 1.43; −1.30 | 1.28; −1.50 | 1.11; −0.84 |

[a] The respective standard deviations are given in parentheses.

**Table S3.** Crystal data and structure refinements of $Na_5M(WO_4)_4$ (M = La, Pr, Sm, Eu, Gd, Tb) determined from powder XRD data via Rietveld refinement[a]

| | $Na_5La(WO_4)_4$ | $Na_5Pr(WO_4)_4$ | $Na_5Sm(WO_4)_4$ | $Na_5Eu(WO_4)_4$ | $Na_5Gd(WO_4)_4$ | $Na_5Tb(WO_4)_4$ |
|---|---|---|---|---|---|---|
| CSD-No. | 1986874 | | | | | |
| $M$ / g mol$^{-1}$ | 1245.21 | 1247.21 | 1256.66 | 1258.26 | 1263.55 | 1265.23 |
| Temperature / K | | | | 300(3) | | |
| Space group | | | | $I4_1/a$ (No. 88) | | |
| $a$ / pm | 1163.319(11) | 1158.140(15) | 1152.270(14) | 1150.503(12) | 1149.044(13) | 1147.108(14) |
| $c$ / pm | 1154.299(13) | 1148.516(17) | 1142.453(16) | 1140.722(14) | 1139.496(15) | 1137.197(16) |
| Volume / $10^6$ pm$^3$ | 1562.13(3) | 1540.49(5) | 1516.86(4) | 1509.92(4) | 1504.48(4) | 1496.39(4) |
| $Z$ | | | | 4 | | |
| $R_{Bragg}$ / % | 2.23 | 1.973 | 1.527 | 1.203 | 1.252 | 0.951 |
| $\rho_{calcd}$ / g cm$^{-3}$ | 5.30 | 5.38 | 5.50 | 5.54 | 5.58 | 5.62 |
| Radiation; wavelength $\lambda$ / Å | | | | $CuK\alpha$; 1.54184 | | |
| Diffractometer | | | | Seifert 3003 TT | | |
| $2\theta$ range / deg | | | | 5–120 | | |
| No. of independent parameters | 49 | 49 | 49 | 49 | 49 | 49 |
| $R_{wp}$ | 0.0375 | 0.0366 | 0.0382 | 0.0253 | 0.029 | 0.02257 |
| Side phase | $NaLa(WO_4)_2$ | $NaPr(WO_4)_2$ | $NaSm(WO_4)_2$ | $NaEu(WO_4)_2$ | $NaGd(WO_4)_2$ | $NaTb(WO_4)_2$ |
| Fraction of side phase / wt.-%[b] | 4.15 | 2.89 | 4.32 | 2.22 | 1.2 | 0.9 |
| Space group | | | | $I4_1/a$ (No. 88) | | |
| $a$ / pm | 535.799(18) | 531.45(3) | 527.10(2) | 525.72(4) | 524.80(8) | 523.09(11) |
| $c$ / pm | 1165.51(7) | 1154.88(13) | 1143.46(10) | 1140.84(17) | 1137.1(3) | 1135.0(5) |
| Volume / $10^6$ pm$^3$ | 334.60(3) | 326.19(6) | 317.70(4) | 315.31(7) | 313.16(13) | 310.58(19) |
| $Z$ | | | | 2 | | |
| $R_{Bragg}$ / % | 1.233 | 1.211 | 1.135 | 0.689 | 1.099 | 0.895 |

[a] The respective standard deviations are given in parentheses. [b] The $NaM(WO_4)_2$ side phase was not refined under a fraction of 1 wt.%.

**Table S4.** Crystal data and structure refinements of $Na_5M(WO_4)_4$ (M = Dy, Ho, Er, Lu, Y) determined from powder XRD data via Rietveld refinement[a]

| | $Na_5Dy(WO_4)_4$ | $Na_5Ho(WO_4)_4$ | $Na_5Er(WO_4)_4$ | $Na_5Lu(WO_4)_4$ | $Na_5Y(WO_4)_4$ |
|---|---|---|---|---|---|
| CSD-No. | | | 1986873 | 1986876 | 1986875 |
| $M$ / g mol$^{-1}$ | 1268.80 | 1271.23 | 1273.56 | 1281.27 | 1195.21 |
| Temperature / K | | | 300(3) | | |
| Space group | | | $I4_1/a$ (No. 88) | | |
| $a$ / pm | 1145.626(15) | 1143.999(12) | 1142.573(13) | 1138.701(12) | 1143.616(11) |
| $c$ / pm | 1135.742(17) | 1134.018(14) | 1132.408(14) | 1128.231(13) | 1134.047(12) |
| Volume / $10^6$ pm$^3$ | 1490.61(4) | 1484.13(4) | 1478.33(4) | 1462.91(3) | 1483.17(3) |
| $Z$ | | | 4 | | |
| $R_{Bragg}$ / % | 1.52 | 1.32 | 1.6 | 1.63 | 1.69 |
| $\rho_{calcd}$ / g cm$^{-3}$ | 5.66 | 5.69 | 5.72 | 5.82 | 5.35 |
| Radiation; wavelength $\lambda$ / Å | | | $CuK\alpha$; 1.54184 Å | | |
| Diffractometer | | | Seifert 3003 TT | | |
| $2\theta$ range / deg | | | 5–120 | | |
| No. of independent parameters | 46 | 46 | 46 | 49 | 46 |
| $R_{wp}$ | 0.0375 | 0.0322 | 0.0394 | 0.036 | 0.0371 |
| Side phase | - | - | - | $NaLu(WO_4)_2$ | - |
| Fraction of side phase / wt.-%[b] | - | - | - | 2.82 | - |
| Space group | - | - | - | $I4_1/a$ (No. 88) | - |
| $a$ / pm | - | - | - | 516.39(3) | - |
| $c$ / pm | - | - | - | 1117.20(11) | - |
| Volume / $10^6$ pm$^3$ | - | - | - | 297.91(4) | - |
| $Z$ | - | - | - | 2 | - |
| $R_{Bragg}$ / % | - | - | - | 1.93 | - |

[a] The respective standard deviations are given in parentheses. [b] The $NaM(WO_4)_2$ side phase was not refined under a fraction of 1 wt.%.
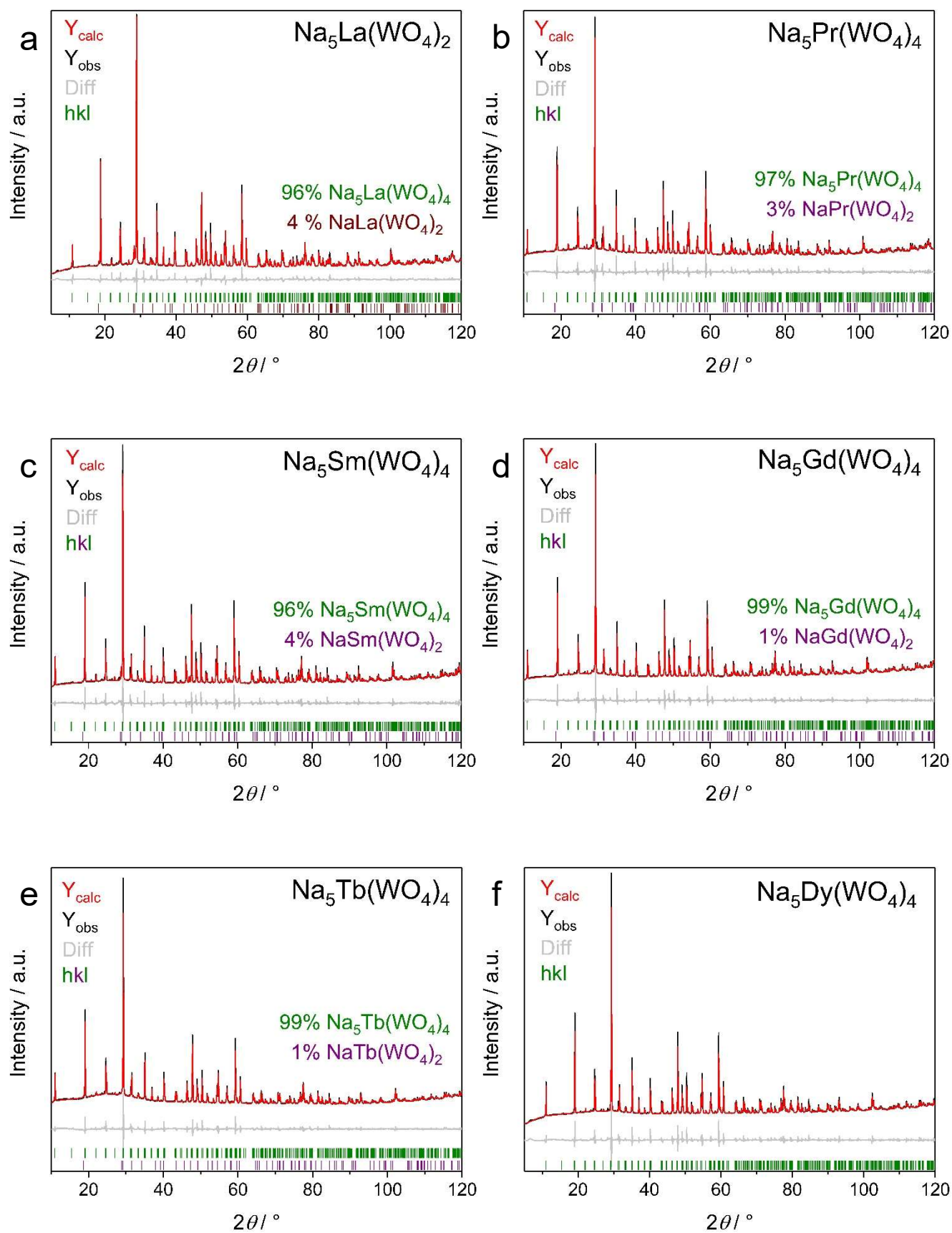
**Fig. S3:** Rietveld refinements of (a) Na₅La(WO₄)₄, (b) Na₅Pr(WO₄)₄, (c) Na₅Sm(WO₄)₄, (d) Na₅Gd(WO₄)₄, (e) Na₅Tb(WO₄)₄ and (f) Na₅Dy(WO₄)₄ prepared by flux synthesis; further details can be found in Tables S3 and S4.
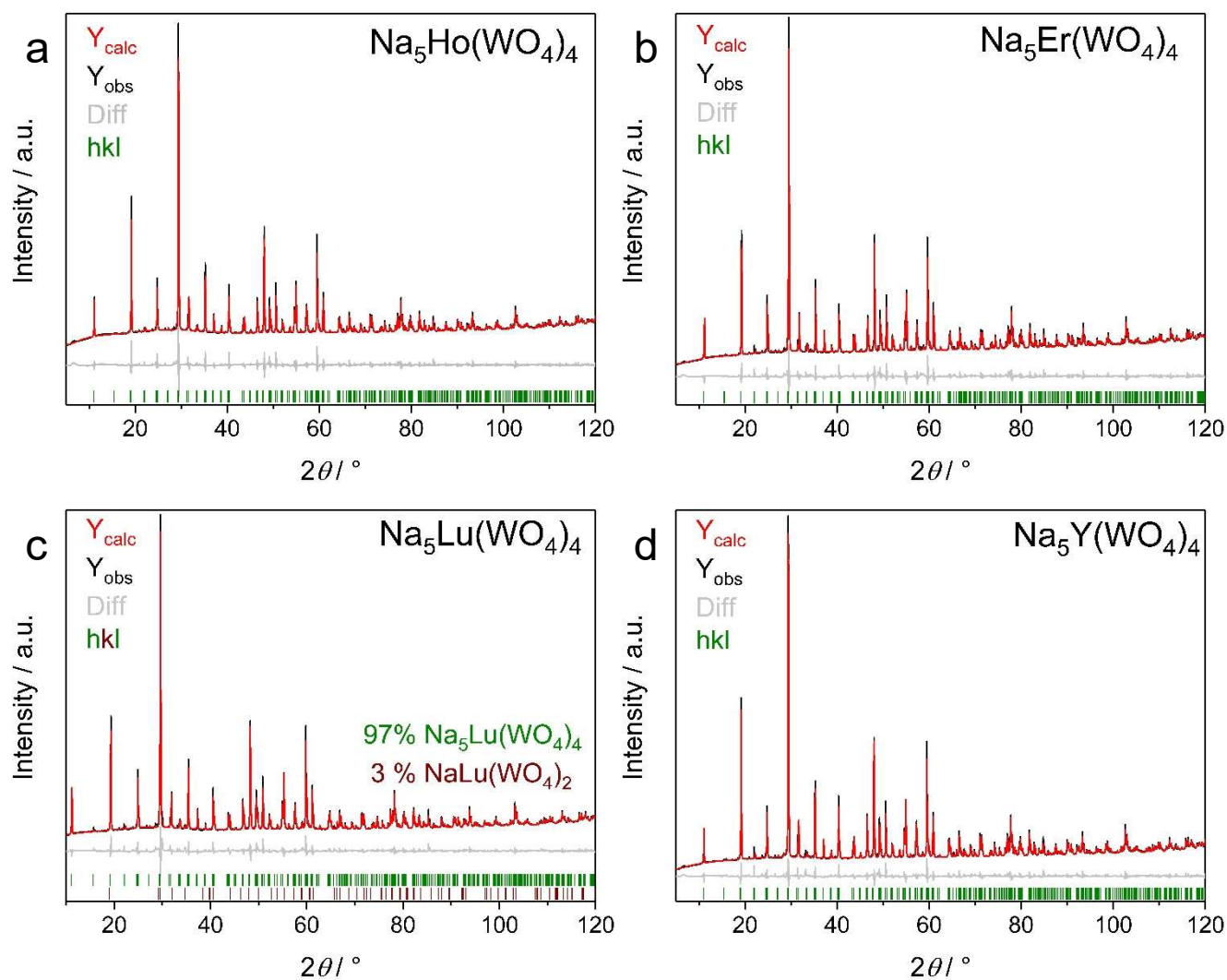
**Fig. S4: Rietveld refinements of (a) Na$_5$Ho(WO$_4$)$_4$, (b) Na$_5$Er(WO$_4$)$_4$, (c) Na$_5$Lu(WO$_4$)$_4$ and (d) Na$_5$Y(WO$_4$)$_4$ prepared by flux synthesis; further details can be found in Table S4.**
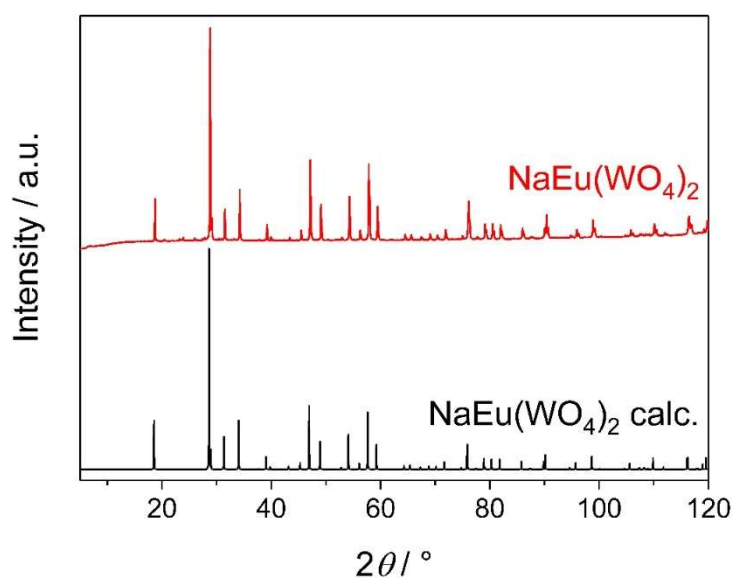


**Fig. S5: Powder XRD pattern of polycrystalline NaEu(WO$_4$)$_2$ compared to a pattern calculated from single crystal data (see Table 1 and S1) showing phase purity.**

**Table S5.** Selected interatomic distances (in pm) and angles (in deg) of $NaEu(WO_4)_2$[a]

| | |
|---|---|
| Na/Eu–O[b] | 245.71(18); 247.67(18) |
| $\sum$ IR (Na/Eu–O)[1] [c] | 248 |
| Na/Eu–Na/Eu | 388.03(1) |
| W–O | 178.97(18) |
| $\sum$ IR (W–O)[1] | 178 |
| O–W–O | 107.13(6); 114.26(12) |

[a] The respective standard deviations are given in parentheses; [b] There are two groups of four oxygen in different distances to cation; [c] The average value of $Na^+$ and $Eu^{3+}$ was used for the sum of ionic radii.
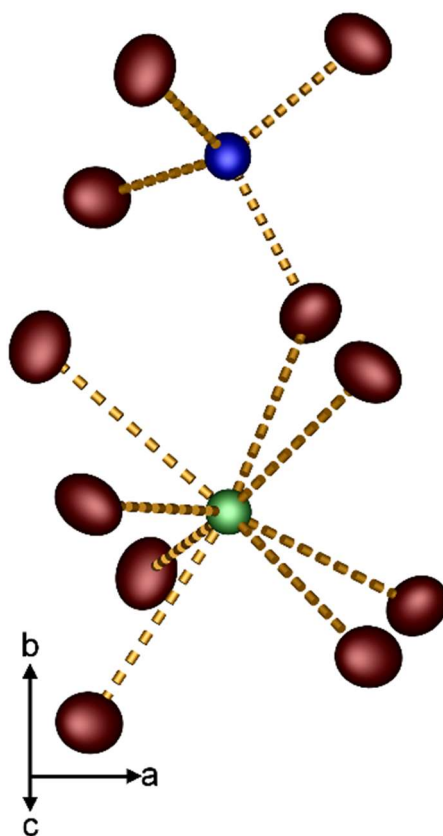


**Fig. S6: Coordination environments of $Na^+$/$Eu^{3+}$(green) and $W^{6+}$(blue) in $NaEu(WO_4)_2$: The former form [(Na/Eu)$O_8$] dodecahedra and the latter $WO_4$ tetrahedra; oxygen is depicted in red; the ellipsoids are shown at 90% probability.**

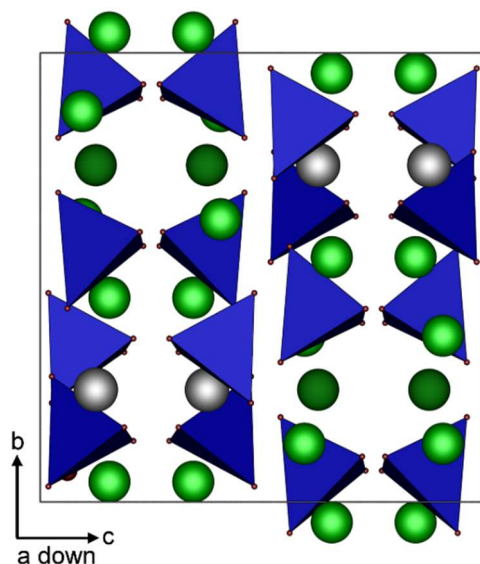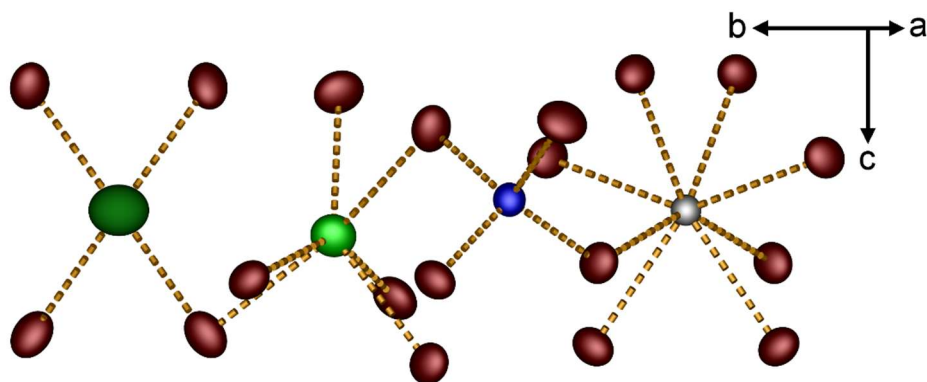**Fig. S7: The unit cell of Na$_5$$M$(WO$_4$)$_4$ with blue WO$_4$ tetrahedra, green Na(1), dark green Na(2)) and grey $M^{3+}$**



**Fig. S8: Coordination environments of Na$^+$ (light green Na(1) and dark green Na(2)) Eu$^{3+}$(grey) and W$^{6+}$(blue) in Na$_5$Eu(WO$_4$)$_4$: they form Na(1)O$_6$ trigonal prisms, Na(2)O$_4$ tetrahedra, WO$_4$ tetrahedra and EuO$_8$ dodecahedra together with oxygen (red), respectively; the ellipsoids are shown at 90% probability.**
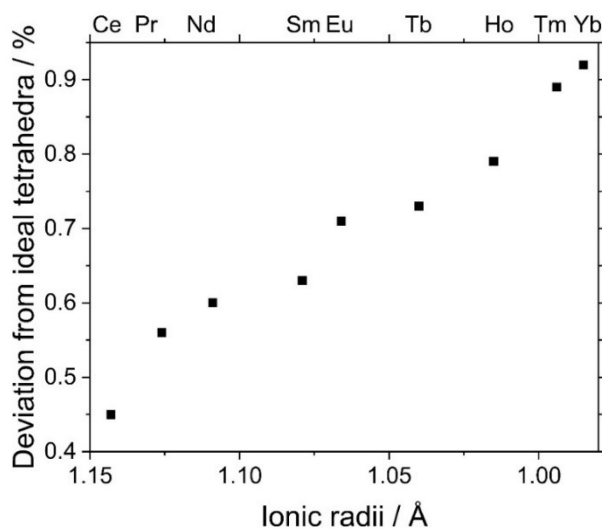


**Fig. S9: The WO$_4$ tetrahedra's deviation from the tetrahedral symmetry calculated by the method of Balic-Zunic[2] and Makovicky[3] is increasing with decreasing ionic radii of $M^{3+}$ in Na$_5$$M$(WO$_4$)$_4$.**

**Table S6.** Selected interatomic distances (in pm), angles (in deg) and the deviation from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ (in %) of $Na_5M(WO_4)_4$ ($M$ = La, Ce, Pr, Nd, Sm)[a]

| | $Na_5La(WO_4)_4$ | $Na_5Ce(WO_4)_4$ | $Na_5Pr(WO_4)_4$ | $Na_5Nd(WO_4)_4$ | $Na_5Sm(WO_4)_4$ |
|---|---|---|---|---|---|
| Data | Rietveld | SC-XRD | SC-XRD | SC-XRD | SC-XRD |
| $M$–O[b] | 238(1)–247(1) | 246.3(7)–247.1(7) | 245.4(2)–245.8(2) | 244.5(3)–244.7(3) | 241.4(2)–241.9(2) |
| $\sum$ IR ($M$–O)[1] | 252 | 250.3 | 248.6 | 246.9 | 243.9 |
| $M$–$M$ | 649.31(1) | 646.98(1) | 646.07(1) | 645.20(2) | 642.73(2) |
| Na(1)-O | 217(1)–275(1) | 228.2(8)–257.7(9) | 228.7(2)–255.8(2) | 229.1(3)–255.2(3) | 228.7(2)–253.1(2) |
| $\sum$ IR (Na(1)–O)[1] [c] | | | 238; 240 | | |
| $\Delta_{octa}$ (Na(1)O$_6$) [d] | | 2.00 | 2.14 | 2.34 | 2.79 |
| Na(2)-O | 239(1) | 247.6(8) | 246.3(2) | 246.4(3) | 245.5(2) |
| $\sum$ IR (Na(2)–O)[1] [c] | | | 237 | | |
| $\Delta_{tetr}$ (Na(2)O$_4$) [d] | | 7.39 | 7.18 | 7.33 | 7.40 |
| W–O | 170(1)–191(1) | 176.5(7)–180.2(7) | 175.6(2)–180.5(2) | 175.6(3)–180.0(3) | 175.9(2)–180.6(2) |
| $\sum$ IR (W–O)[1] [c] | | | 178; 180 | | |
| O–W–O | 103.0(6)–116.2(5) | 106.5(3)–113.3(3) | 106.2(1)–113.4(1) | 105.9(1)–113.5(1) | 105.9(1)–113.7(1) |
| $\Delta_{tetr}$ (WO$_4$)[d] | - | 0.45 | 0.56 | 0.6 | 0.63 |
| $M$–O–W | 130.9(6)–137.0(6) | 129.1(3)–130.4(4) | 129.3(1)–130.2(1) | 129.4(2)–130.3(1) | 129.3(1)–130.3(1) |

[a] The respective standard deviations are given in parentheses. The standard deviations from Rietveld refinement are numerical standard deviations as obtained from the refinement and do not necessarily represent an interval of trust.; [b] There are two distinct pairs of $M$-O distances. [c] Different sums of ionic radii due to oxygen with both CN = 3 and 4. [d] The deviation of the NaO$_6$ octahedra, NaO$_4$ tetrahedra and WO$_4$ tetrahedra from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ was calculated by the Balic-Zunic[2] and Makovicky[3] for all structures derived from single-crystal XRD data.

**Table S7.** Selected interatomic distances (in pm), angles (in deg) and deviation from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ (in %) of $Na_5M(WO_4)_4$ ($M$ = Eu, Gd, Tb, Dy, Ho)[a]

| | $Na_5Eu(WO_4)_4$ | $Na_5Gd(WO_4)_4$ | $Na_5Tb(WO_4)_4$ | $Na_5Dy(WO_4)_4$ | $Na_5Ho(WO_4)_4$ |
|---|---|---|---|---|---|
| Data | SC-XRD | SC-XRD | SC-XRD | Rietveld | SC-XRD |
| $M$–O[b] | 240.3(2)–240.7(2) | 239.2(2)–239.2(2) | 238.2(3)–238.8(3) | 222(2)–238(2) | 236.0(2)–237.1(2) |
| $\sum$ IR ($M$–O)[1] | 242.6 | 241.3 | 240 | 238.7 | 237.5 |
| $M$–$M$ | 641.81(2) | 640.20(2) | 640.13(2) | 639.32(1) | 638.47(2) |
| Na(1)-O | 229.3(2)–252.3(2) | 228.9(2)–251.2(3) | 229.6(3)–250.7(3) | 226(2)–265(2) | 229.6(3)– 249.6(3) |
| $\sum$ IR (Na(1)–O)[1] [c] | | | 238; 240 | | |
| $\Delta_{octa}$ (Na(1)O$_6$) [d] | 2.97 | 3.33 | 3.78 | | 3.97 |
| Na(2)-O | 245.0(2) | 245.0(2) | 244.9(3) | 242(2) | 243.9(2) |
| $\sum$ IR (Na(2)–O)[1] | | | 237 | | |
| $\Delta_{tetr}$ (Na(2)O$_4$) [d] | 7.53 | 7.48 | 7.67 | | 7.81 |
| W–O | 175.6(2)–180.7(2) | 175.6(2)–181.0(2) | 175.4(3)–180.6(3) | 170(2)–191(2) | 175.6(2)– 180.6(2) |
| $\sum$ IR (W–O)[1] [c] | | | 178; 180 | | |
| O–W–O | 105.6(1)–113.8(1) | 107.1(1)–113.7(1) | 105.5(1)–113.8(1) | 97.7(9)–115.9(8) | 105.3(1)–114.0(1) |
| $\Delta_{tetr}$ (WO$_4$) [d] | 0.71 | 0.75 | 0.73 | | 0.79 |
| $M$–O–W | 129.4(1)–130.1(1) | 129.4(1)–130.0(1) | 129.5(1)–130.2(1) | 133(1)–133.5(9) | 129.5(1)–130.0(1) |

[a] The respective standard deviations are given in parentheses. The standard deviations from Rietveld refinement are numerical standard deviations as obtained from the refinement and do not necessarily represent an interval of trust.; [b] There are two distinct pairs of $M$-O distances. [c] Different sums of ionic radii due to oxygen with both CN = 3 and 4. [d] The deviation of the NaO$_6$ octahedra, NaO$_4$ tetrahedra and WO$_4$ tetrahedra from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ was calculated by the Balic-Zunic[2] and Makovicky[3] for all structures derived from single-crystal XRD data.

**Table S8.** Selected interatomic distances (in pm), angles (in deg) and deviation from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ (in %) of $Na_5M(WO_4)_4$ ($M$ = Er, Tm, Yb)[a]

| Data | $Na_5Er(WO_4)_4$ Rietveld | $Na_5Tm(WO_4)_4$ SC-XRD | $Na_5Yb(WO_4)_4$ SC-XRD |
|---|---|---|---|
| $M$–O[b] | 232(1)–243(1) | | 233.3(3)– 234.7(3) |
| $\sum$ IR ($M$–O)[1] | 236.4 | 235.4 | 234.5 |
| $M$–$M$ | 637.59(1) | 636.14(3) | 635.93(5) |
| Na(1)-O | 208(1)–264(2) | 228.9(3)–247.7(3) | 229.6(3)– 247.2(3) |
| $\sum$ IR (Na(1)–O)[1][c] | | 238; 240 | |
| $\Delta_{octa}$ (Na(1)O$_6$) [d] | | 4.53 | 4.37 |
| Na(2)-O | 228(2) | 243.1(2) | 243.5(3) |
| $\sum$ IR (Na(2)–O)[1] | | 237 | |
| $\Delta_{tetr}$ (Na(2)O$_4$) [d] | | 7.77 | 8.01 |
| W–O | 170(1)– 191(2) | 175.3(2)– 181.0(2) | 175.7(3)–181.0(3) |
| $\sum$ IR (W–O)[1][c] | | 178; 180 | |
| O–W–O | 98.6(7)–116.5(7) | 105.2(1)–114.1(1) | 104.9(1)–114.3(1) |
| $\Delta_{tetr}$ (WO$_4$) [d] | - | 0.89 | 0.92 |
| $M$–O–W | 130.7(7)–131.7(8) | 129.4(1)–129.9(1) | 129.3(1)–129.6(1) |

[a] The respective standard deviations are given in parentheses. The standard deviations from Rietveld refinement are numerical standard deviations as obtained from the refinement and do not necessarily represent an interval of trust.; [b] There are two distinct pairs of $M$-O distances. [c] Different sums of ionic radii due to oxygen with both CN = 3 and 4. [d] The deviation of the NaO$_6$ octahedra, NaO$_4$ tetrahedra and WO$_4$ tetrahedra from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ was calculated by the method of Balic-Zunic[2] and Makovicky[3] for all structures derived from single-crystal XRD data.

**Table S9.** Selected interatomic distances (in pm), angles (in deg) and deviation from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ (in %) of $Na_5M(WO_4)_4$ ($M$ = Lu, Y, Bi)[a]

| Data | $Na_5Lu(WO_4)_4$ Rietveld | $Na_5Y(WO_4)_4$ Rietveld | $Na_5Bi(WO_4)_4$ SC-XRD |
|---|---|---|---|
| $M$–O[b] | 226(1)–238(1) | 228(1)–243(1) | 243.7(4)–244.5(4) |
| $\sum$ IR ($M$–O)[1] | 233.7 | 237.9 | 234.5 |
| $M$–$M$ | 635.39(1) | 638.23(1) | 643.85(2) |
| Na(1)-O | 212(2)– 269(2) | 218(1)–258(2) | 228.8(4)–253.4(4) |
| $\sum$ IR (Na(1)–O)[1][c] | | 238; 240 | |
| $\Delta_{octa}$ (Na(1)O$_6$) [d] | | | 2.17 |
| Na(2)-O | 237(2) | 242(1) | 245.8(4) |
| $\sum$ IR (Na(2)–O)[1] | | 237 | |
| $\Delta_{tetr}$ (Na(2)O$_4$) [d] | | | 7.49 |
| W–O | 172(1)–190(1) | 164(1)–189(1) | 175.3(4)–180.5(4) |
| $\sum$ IR (W–O)[1][c] | | 178; 180 | |
| O–W–O | 98.5(7)–119.8(6) | 99.8(6)–114.6(5) | 105.3(2)–114.1(2) |
| $\Delta_{tetr}$ (WO$_4$) [d] | - | - | 0.71 |
| $M$–O–W | 130.2(7)–131.2(7) | 130.2(6)–135.2(6) | 128.5(2)–129.3(2) |

[a] The respective standard deviations are given in parentheses. The standard deviations from Rietveld refinement are numerical standard deviations as obtained from the refinement and do not necessarily represent an interval of trust.; [b] There are two distinct pairs of $M$-O distances. [c] Different sums of ionic radii due to oxygen with both CN = 3 and 4. [d] The deviation of the NaO$_6$ octahedra, NaO$_4$ tetrahedra and WO$_4$ tetrahedra from the ideal symmetry $\Delta_{octa}$ or $\Delta_{tetr}$ was calculated by the method of Balic-Zunic[2] and Makovicky[3] for all structures derived from single-crystal XRD data.
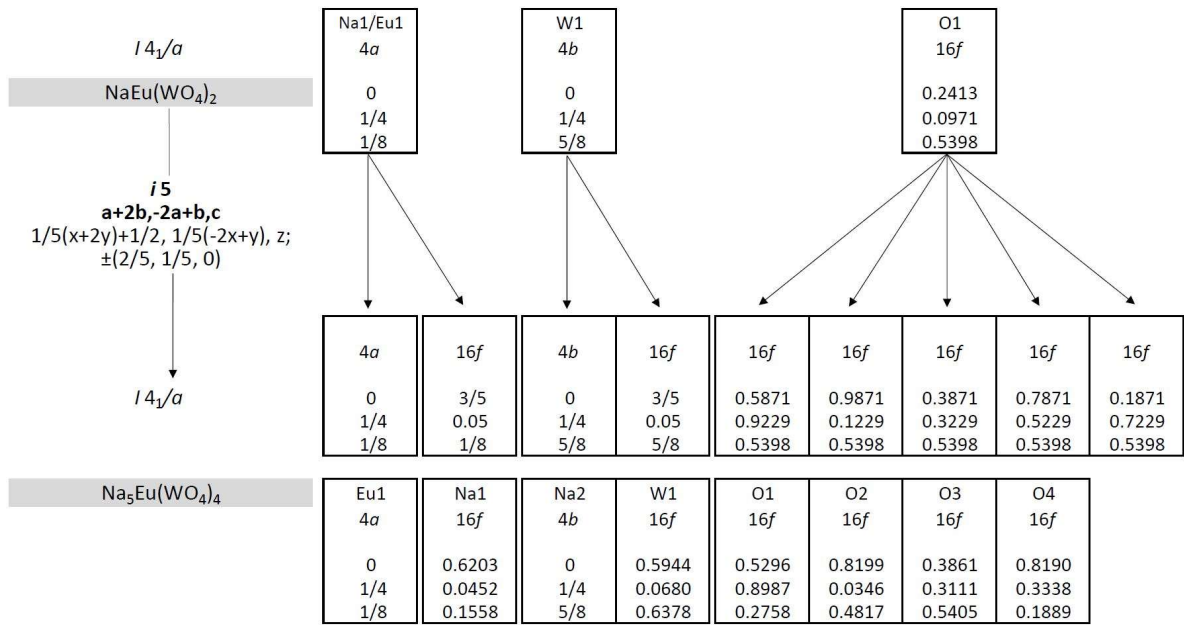
$I\,4_1/a$

| Na1/Eu1 | W1 | O1 |
|---|---|---|
| 4a | 4b | 16f |
| 0 | 0 | 0.2413 |
| 1/4 | 1/4 | 0.0971 |
| 1/8 | 5/8 | 0.5398 |

NaEu(WO$_4$)$_2$

**i 5**
**a+2b,-2a+b,c**
1/5(x+2y)+1/2, 1/5(-2x+y), z;
±(2/5, 1/5, 0)

$I\,4_1/a$

| 4a | 16f | 4b | 16f | 16f | 16f | 16f | 16f | 16f |
|---|---|---|---|---|---|---|---|---|
| 0 | 3/5 | 0 | 3/5 | 0.5871 | 0.9871 | 0.3871 | 0.7871 | 0.1871 |
| 1/4 | 0.05 | 1/4 | 0.05 | 0.9229 | 0.1229 | 0.3229 | 0.5229 | 0.7229 |
| 1/8 | 1/8 | 5/8 | 5/8 | 0.5398 | 0.5398 | 0.5398 | 0.5398 | 0.5398 |

Na$_5$Eu(WO$_4$)$_4$

| Eu1 | Na1 | Na2 | W1 | O1 | O2 | O3 | O4 |
|---|---|---|---|---|---|---|---|
| 4a | 16f | 4b | 16f | 16f | 16f | 16f | 16f |
| 0 | 0.6203 | 0 | 0.5944 | 0.5296 | 0.8199 | 0.3861 | 0.8190 |
| 1/4 | 0.0452 | 1/4 | 0.0680 | 0.8987 | 0.0346 | 0.3111 | 0.3338 |
| 1/8 | 0.1558 | 5/8 | 0.6378 | 0.2758 | 0.4817 | 0.5405 | 0.1889 |

**Fig. S10: Group–subgroup scheme in the Bärnighausen formalism[4,5] showing the symmetry relation between Na$_5$Eu(WO$_4$)$_4$ and NaEu(WO$_4$)$_2$.**

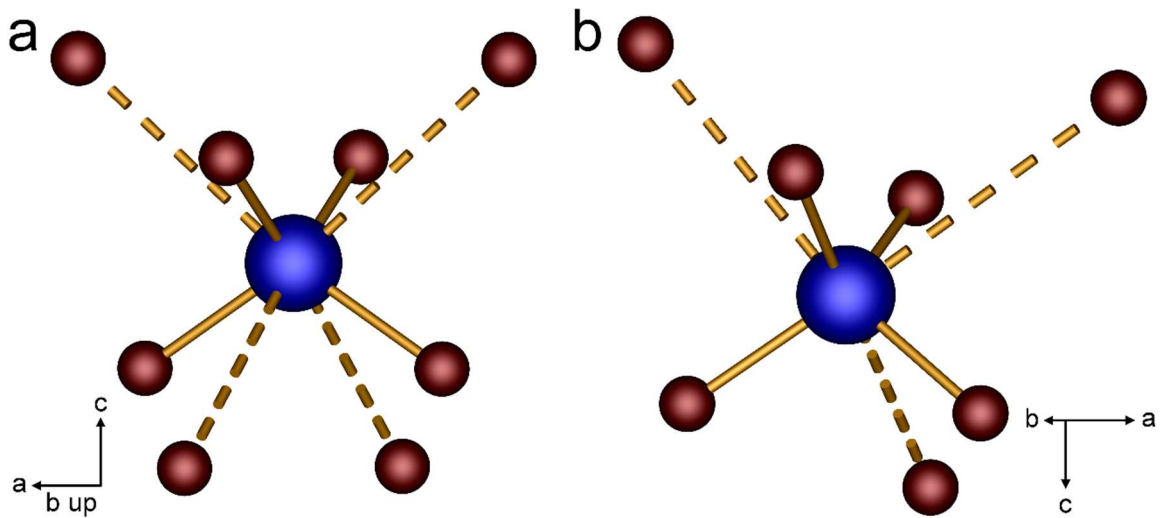

**Fig. S11: Coordination environments of W$^{6+}$ (blue) in (a) NaEu(WO$_4$)$_2$ and (b) Na$_5$Eu(WO$_4$)$_4$: they differ in the second coordination sphere; the WO$_4$ tetrahedra in the first coordination sphere are tetracapped and tricapped in the second coordination sphere, respectively; oxygen is depicted in red, tungsten in blue.**
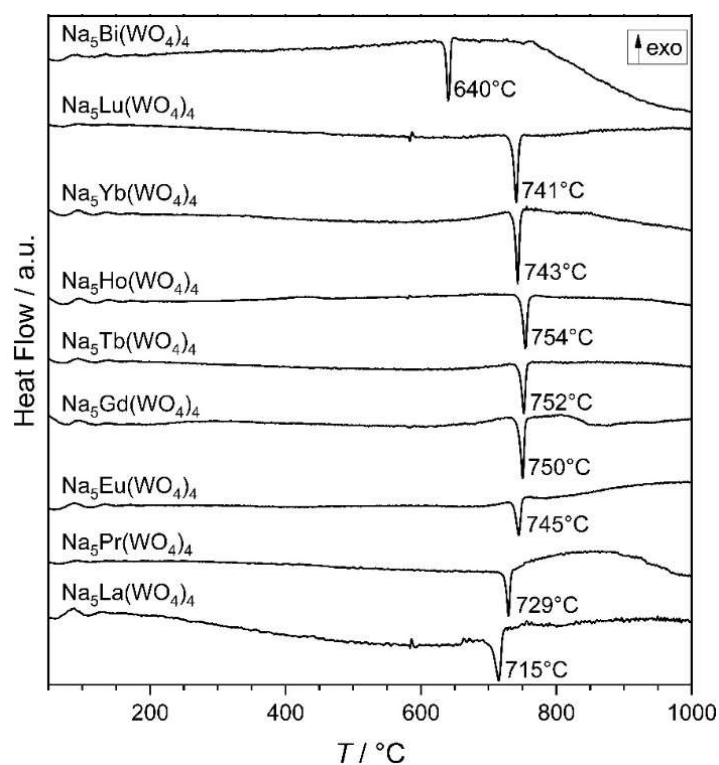
**Fig. S12: DSC signals of Na$_5$$M$(WO$_4$)$_4$ ($M$ = La, Pr, Eu, Gd, Tb, Ho, Yb, Lu, Bi): all samples show one endothermic peak related to the simultaneous melting and decomposition point labelled with the temperature of the peaks' maxima ($T_d$).**
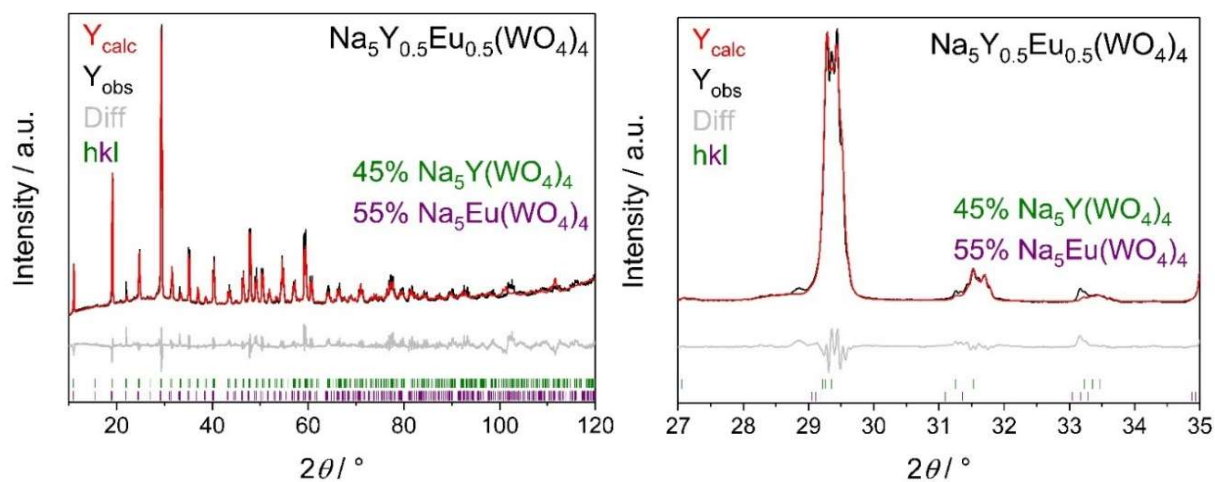


**Fig. S13: Rietveld refinement of Na$_5$Y$_{0.5}$Eu$_{0.5}$(WO$_4$)$_4$ prepared via the flux synthesis with 500% Na$_2$WO$_4$ surplus showing a phase mixture of 45% Na$_5$Y(WO$_4$)$_4$ and 55% Na$_5$Eu(WO$_4$)$_4$: details can be found in Table S12; the enlarged depiction on the right shows the splitting of the mainreflection at $2\theta \approx 29.5°$.**

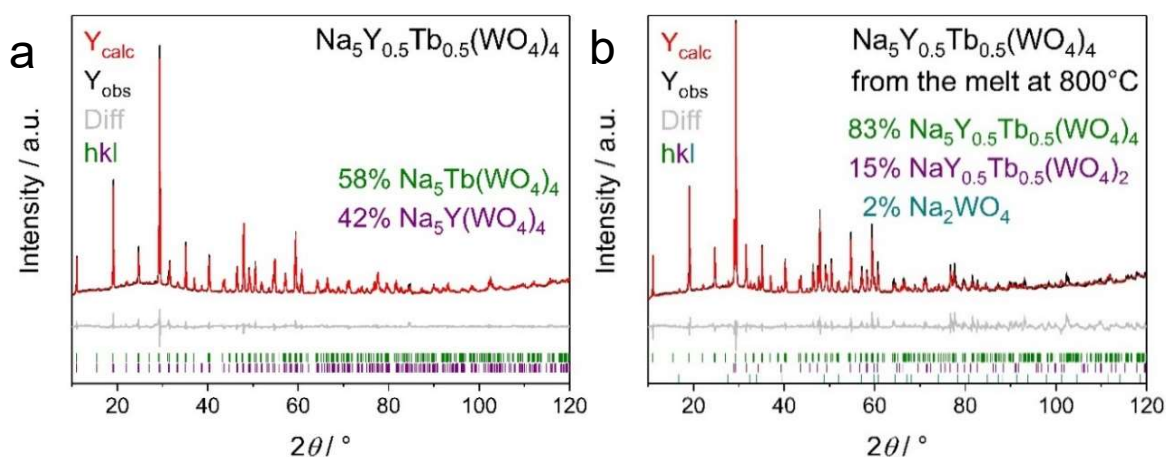**Fig. S14: (a)** Rietveld refinement of $Na_5Y_{0.5}Tb_{0.5}(WO_4)_4$ prepared via the synthesis with 500% $Na_2WO_4$ surplus showing a phase mixture of 58% $Na_5Y(WO_4)_4$ and 42% $Na_5Eu(WO_4)_4$ and **(b)** of $Na_5Y_{0.5}Tb_{0.5}(WO_4)_4$ after subsequent melting at 800°C in a Pt crucible showing a phase mixture of 83% $Na_5Y_{0.5}Tb_{0.5}(WO_4)_4$, 15% $NaY_{0.5}Tb_{0.5}(WO_4)_2$ and 2% $Na_2WO_4$: details can be found in Table S12.



**Fig. S15:** Rietveld refinement of $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ prepared via the synthesis with 500% $Na_2WO_4$ surplus and subsequently melted at 800°C in a Pt crucible showing a phase mixture of 83% $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$, 15% $NaY_{0.5}Eu_{0.5}(WO_4)_2$ and 2% $Na_2WO_4$: details can be found in Table S12; the enlarged depiction on the right shows the non-splitting of the mainreflection at $2\theta \approx 29.5°$.
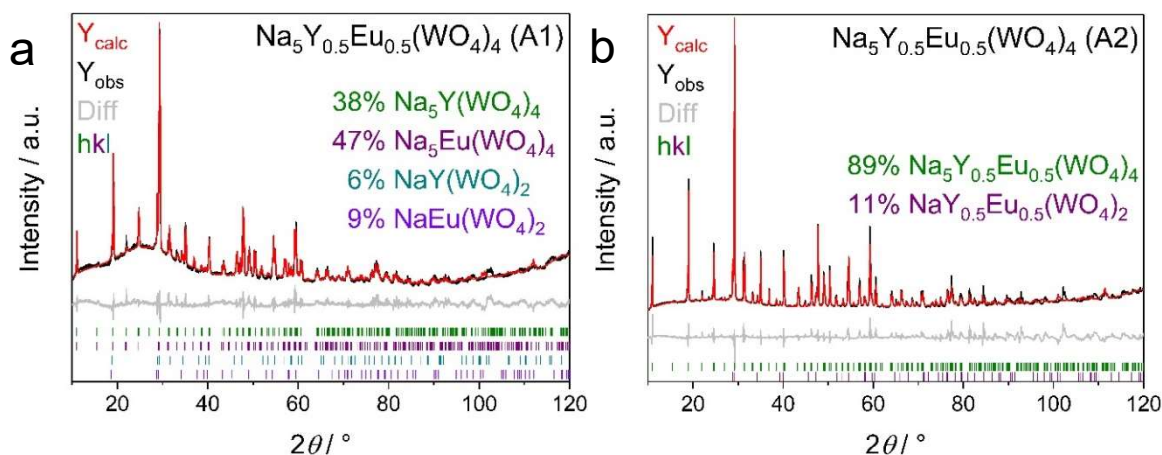


**Fig. S16:** Rietveld refinement of $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ prepared via solid state syntheses A1 **(a)** and A2 **(b)**: The product of synthesis A1 consists of a phase mixture of 38% $Na_5Y(WO_4)_4$, 47% $Na_5Eu(WO_4)_4$, 6% $NaY(WO_4)_2$ and 9% $NaEu(WO_4)_2$, while the sample prepared via A2 shows only two phases of 89% $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ and 11% $NaY_{0.5}Eu_{0.5}(WO_4)_2$; details can be found in Table S12.

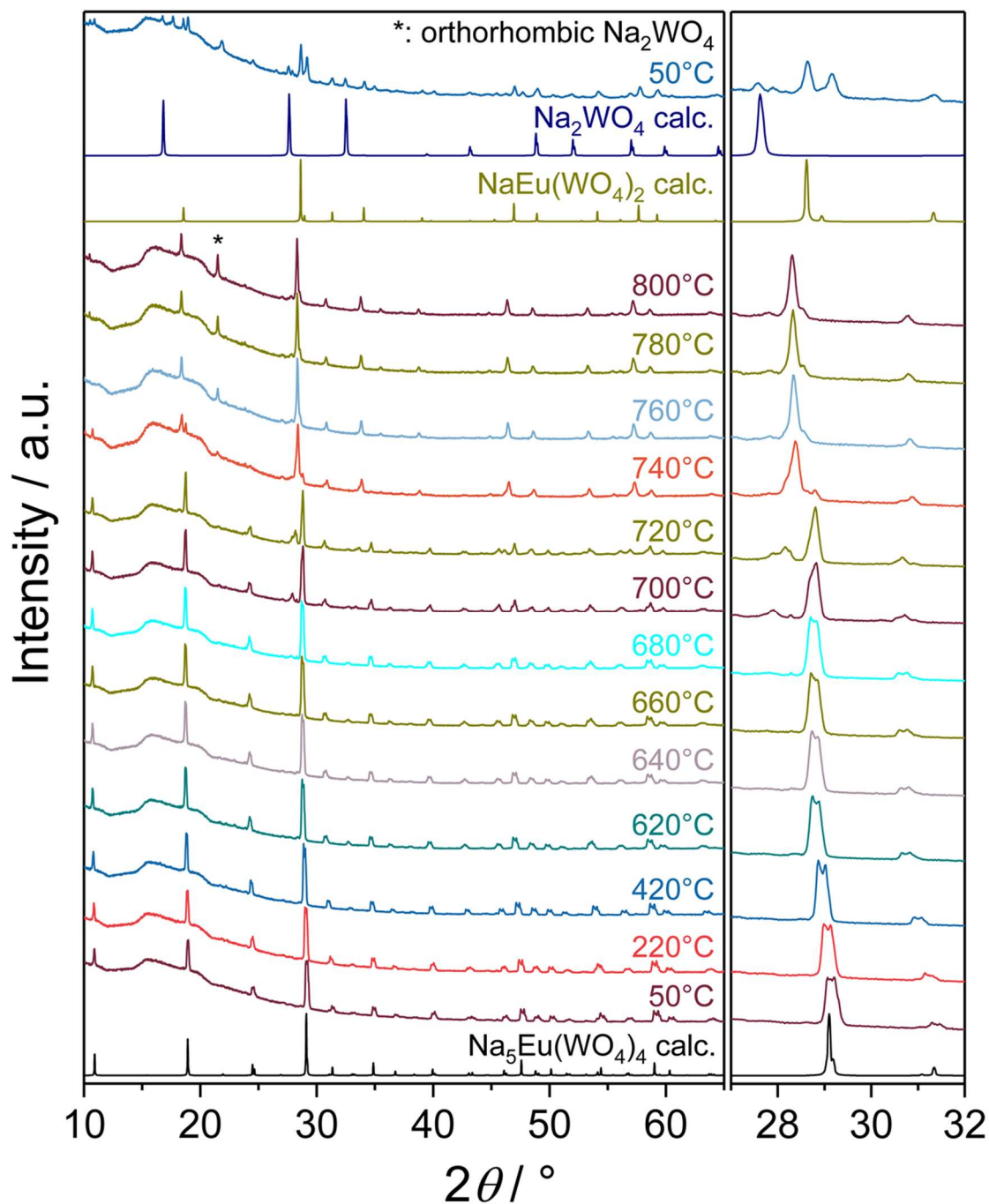**Fig. S17:** Variable temperature powder XRD patterns of $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ prepared via the flux synthesis with 500% $Na_2WO_4$ surplus compared to theoretical patterns calculated from the single crystal data for $Na_5Eu(WO_4)_4$ and $NaEu(WO_4)_2$ plus from literature for $Na_2WO_4$:[6] the pattern show the closing of the miscibility gap between 680°C and 720°C with the double reflection around $2\theta=29°$ becoming a single reflection as well as the decomposition into $NaY_{0.5}Eu_{0.5}(WO_4)_2$ and $Na_2WO_4$ starting around 700°C; moreover, the reflexes related to $Na_2WO_4$ disappear above 720°C due to the melting of this phase; there is an experimental offset between the furnace temperatures displayed in the graph and the actual temperature at the sample of approximately 20°C; the additional reflection at $2\theta=21.5°$ marked with a black asterisk could be assigned to the orthorhombic high-temperature modification of $Na_2WO_4$ reported by Pistorius.[7]

**Table S10.** Structural data from the Rietveld refinement on $Na_5Y_{1-x}Eu_x(WO_4)_4$ and $Na_5Y_{1-y}Tb_y(WO_4)_4$[a, b]

| | $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ | $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ M[c] | $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ (A1) | $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ (A2) | $Na_5Y_{0.5}Tb_{0.5}(WO_4)_4$ | $Na_5Y_{0.5}Tb_{0.5}(WO_4)_4$ M[c] |
|---|---|---|---|---|---|---|
| $R_{wp}$ | 0.04434 | 0.04029 | 0.02439 | 0.05042 | 0.02004 | 0.04092 |
| No. of independent parameters | 44 | 42 | 49 | 43 | 45 | 46 |
| Temperature / K | 300(3) | | | | | |
| Radiation; wavelength $\lambda$ / Å | $CuK\alpha$; 1.54184 | | | | | |
| Diffractometer | Seifert 3003 TT | | | | | |
| $2\theta$ range / deg | 5–120 | | | | | |
| First Phase | $Na_5Y(WO_4)_4$ | $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ | $Na_5Y(WO_4)_4$ | $Na_5Y_{0.5}Eu_{0.5}(WO_4)_4$ | $Na_5Y(WO_4)_4$ | $Na_5Y_{0.5}Tb_{0.5}(WO_4)_4$ |
| Fraction of first phase / wt.-% | 45 | 83 | 38 | 89 | 42 | 83 |
| $a$ / pm | 1143.70(2) | 1146.879(14) | 1143.60(2) | 1146.315(17) | 1143.562(16) | 1145.023(18) |
| $c$ / pm | 1134.14(3) | 1137.303(15) | 1134.40(4) | 1138.78(2) | 1133.83(2) | 1135.50(2) |
| Volume / $10^6$ $pm^3$ | 1483.50(7) | 1495.93(4) | 1483.58(8) | 1496.40(6) | 1482.75(5) | 1488.73(6) |
| $R_{Bragg}$ / % | 2.279 | 2.263 | 1.088 | 3.254 | 1.036 | 2.224 |
| Second Phase | $Na_5Eu(WO_4)_4$ | $NaY_{0.5}Eu_{0.5}(WO_4)_2$ | $Na_5Eu(WO_4)_4$ | $NaY_{0.5}Eu_{0.5}(WO_4)_2$ | $Na_5Tb(WO_4)_4$ | $NaY_{0.5}Tb_{0.5}(WO_4)_2$ |
| Fraction of second phase / wt.-% | 55 | 15 | 47 | 11 | 58 | 15 |
| $a$ / pm | 1149.57(2) | 523.357(14) | 1149.05(2) | 522.89(5) | 1146.404(15) | 521.938(19) |
| $c$ / pm | 1140.25(4) | 1133.64(6) | 1140.18(4) | 1134.2(2) | 1136.631(18) | 1129.70(8) |
| Volume / $10^6$ $pm^3$ | 1506.86(8) | 310.51(2) | 1505.38(7) | 310.10(8) | 1493.81(5) | 307.75(3) |
| $R_{Bragg}$ / % | 3.033 | 1.963 | 1.462 | 1.995 | 0.897 | 1.787 |
| Third phase | | $Na_2WO_4$[d] | $NaY(WO_4)_2$ | | | $Na_2WO_4$[d] |
| Fraction of third phase / wt.-% | | 2 | 6 | | | 2 |
| $a$ / pm | | 912.80(5) | 520.67(4) | | | 913.29(7) |
| $c$ / pm | | 912.80(5) | 1127.27(15) | | | 913.29(7) |
| Volume / $10^6$ $pm^3$ | | 760.54(13) | 305.60(6) | | | 761.78(17) |
| $R_{Bragg}$ / % | | 1.968 | 1.250 | | | 1.543 |
| Forth phase | | | $NaEu(WO_4)_2$ | | | |
| Fraction of forth phase / wt.-% | | | 9 | | | |
| $a$ / pm | | | 525.15(3) | | | |
| $c$ / pm | | | 1138.43(11) | | | |
| Volume / $10^6$ $pm^3$ | | | 313.95(4) | | | |
| $R_{Bragg}$ / % | | | 1.025 | | | |

[a] The respective standard deviations are given in parentheses. [b] Unless specified differently, all phases crystallise in space group $I4_1/a$ (No. 88) with $Z = 4$ for all $Na_5M(WO_4)_4$ phases and $Z = 2$ for all $NaM(WO_4)_2$ phases, respectively. [c] The suffix M symbolises the samples obtained from the melt at 800°C. [d] $Na_2WO_4$ crystallises in space group $Fd\bar{3}m$ (No. 227) with $Z = 8$.

**Table S11.** Crystal data and structure refinements of $Na_5Y_{0.49}Eu_{0.51}(WO_4)_4$ and $Na_5Y_{0.49}Tb_{0.51}(WO_4)_4$ determined from single-crystal data[a]

| | $Na_5Y_{0.49}Eu_{0.51}(WO_4)_4$ | $Na_5Y_{0.49}Tb_{0.51}(WO_4)_4$ |
|---|---|---|
| CSD-No. | 1986865 | 19868560 |
| $M$ / g mol$^{-1}$ | 1228.23 | 1231.29 |
| Crystal size / mm$^3$ | 0.05 × 0.02 × 0.02 | 0.05 × 0.03 × 0.03 |
| Temperature / K | 300(3) | |
| Space group | $I4_1/a$ (No. 88) | |
| $a$ / pm | 1146.81(4) | 1146.02(2) |
| $c$ / pm | 1137.59(4) | 1136.78(3) |
| Volume / $10^6$ pm$^3$ | 1496.13(12) | 1493.00(7) |
| $Z$ | 4 | |
| $\rho_{calcd}$ / g cm$^{-3}$ | 5.45 | 5.47 |
| Absorption coefficient $\mu$ / mm$^{-1}$ | 34.9 | 35.2 |
| $F(000)$ / $e$ | 2120 | 2124 |
| Radiation; wavelength $\lambda$ / Å | Mo$K\alpha$; 0.71073 | |
| Diffractometer | Bruker D8 Venture | |
| Absorption correction | Multi-scan | |
| Transmission (min; max) | 0.6078; 0.7475 | 0.4460; 0.7491 |
| Index range $h|k|l$ | −20/20|−20/19|−19/19 | −21/21|−21/21|−21/21 |
| $\theta$ range / deg | 2.522–38.483 | 2.524–42.492 |
| Reflections collected | 26544 | 20167 |
| Independent reflections | 2103 | 2682 |
| $R_{int}$ | 0.0633 | 0.0221 |
| Obs. reflections ($I > 2\,\sigma(I)$) | 1822 | 2438 |
| Refined parameters | 61 | 61 |
| $R_1$ (all data) | 0.0271 | 0.021 |
| $wR_2$ (all data) | 0.0325 | 0.0311 |
| GooF | 1.054 | 1.113 |
| Residual electron density (max; min) / $e^-$ | 1.68; -1.45 | 1.28; -1.14 |

[a] The respective standard deviations are given in parentheses.
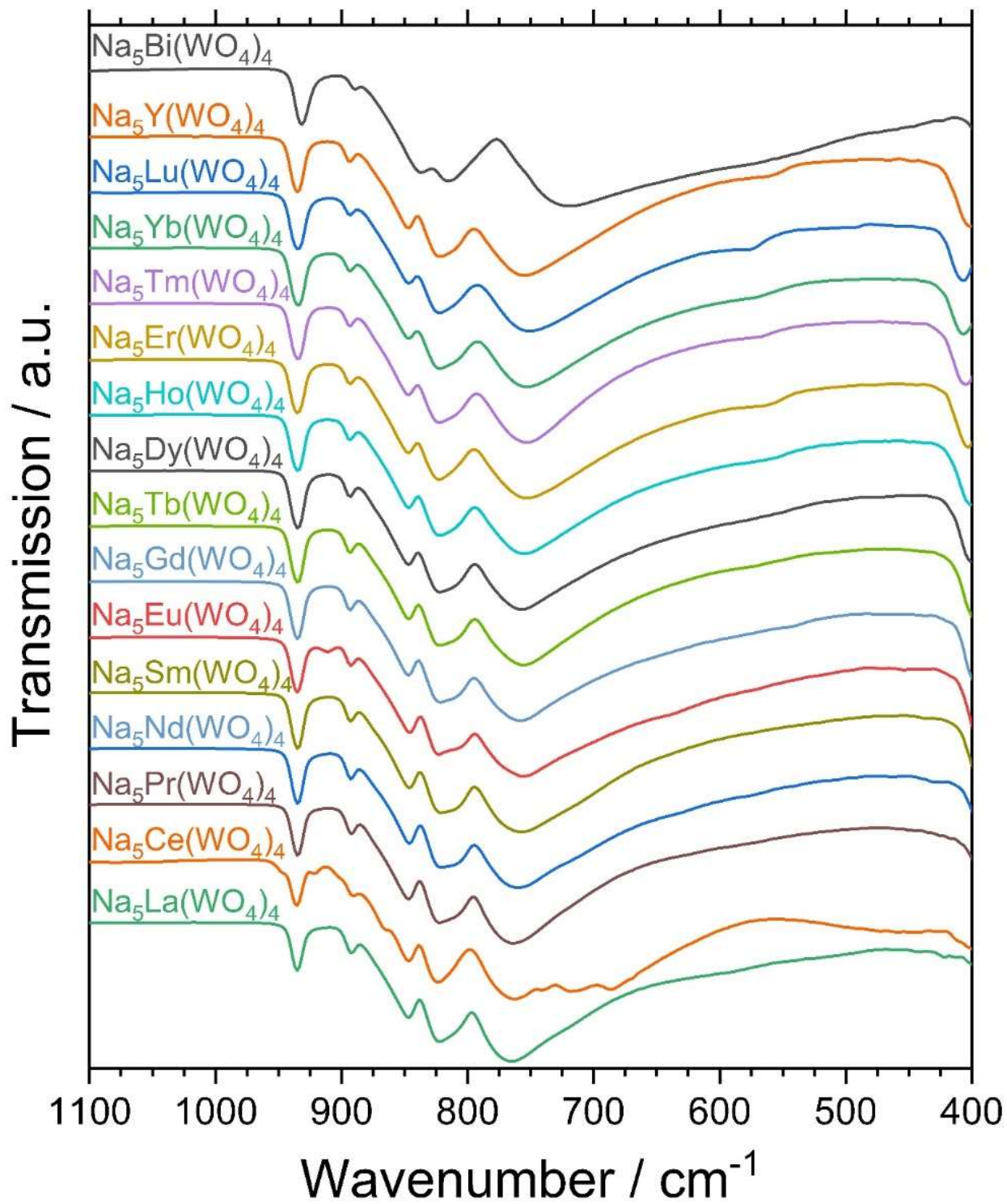
**Fig.S18: FTIR spectra of Na₅*M*(WO₄)₄ (*M* = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Bi)**

Fig.S19: UV/Vis spectra of Na₅*M*(WO₄)₄ (*M* = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Bi)

**Table S12.** Assignment of absorption bands in UV/Vis spectra of Na$_5$M(WO$_4$)$_4$ besides the O$^{2-}$-W$^{6+}$ LMCT found between 230 nm and 250 nm for all samples.[8,9,10,11,12,13,14,15,16,17,18 a]

| Na$_5$Ce(WO$_4$)$_4$ | Wavelength λ / nm | Energy E / cm$^{-1}$ | Transition |
|---|---|---|---|
| | 350 | 28571 | 4f-5d |
| **Na$_5$Pr(WO$_4$)$_4$** | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 449 | 22272 | $^3H_4 \rightarrow {}^1I_6$ |
| | 474 | 21097 | $^3H_4 \rightarrow {}^3P_1$ |
| | 487 | 20534 | $^3H_4 \rightarrow {}^3P_0$ |
| | 587 | 17036 | $^3H_4 \rightarrow {}^1D_2$ |
| | 595 | 16807 | $^3H_4 \rightarrow {}^1D_2$ |
| | 609 | 16420 | $^3H_4 \rightarrow {}^1D_2$ |
| **Na$_5$Nd(WO$_4$)$_4$** | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 353 | 28329 | $^4I_{9/2} \rightarrow {}^2I_{11/2}$ |
| | 360 | 27778 | $^4I_{9/2} \rightarrow {}^4D_{3/2}$ |
| | 422 | 23697 | $^4I_{9/2} \rightarrow {}^2D_{5/2}$ |
| | 432; 435 | 23148 | $^4I_{9/2} \rightarrow {}^2P_{1/2}$ |
| | 461 | 21692 | $^4I_{9/2} \rightarrow {}^4G_{11/2}, ({}^2D,{}^2F)_{3/2}$ |
| | 473 | 21142 | $^4I_{9/2} \rightarrow {}^2G_{9/2}$ |
| | 480 | 20833 | $^4I_{9/2} \rightarrow {}^2K_{15/2}$ |
| | 517 | 19342 | $^4I_{9/2} \rightarrow {}^4G_{9/2}$ |
| | 527; 532 | 18975 | $^4I_{9/2} \rightarrow {}^4G_{7/2}$ |
| | 576; 583, 587 | 17361 | $^4I_{9/2} \rightarrow {}^2G_{7/2}$ |
| | 594 | 16835 | $^4I_{9/2} \rightarrow {}^4G_{5/2}$ |
| | 631 | 15848 | $^4I_{9/2} \rightarrow {}^2H_{11/2}$ |
| | 677, 688 | 14771 | $^4I_{9/2} \rightarrow {}^4F_{9/2}$ |
| | 741 | 13495 | $^4I_{9/2} \rightarrow {}^5S_{3/2}$ |
| | 752 | 13298 | $^4I_{9/2} \rightarrow {}^4F_{7/2}$ |
| | 791 | 12642 | $^4I_{9/2} \rightarrow {}^2H_{9/2}$ |
| **Na$_5$Sm(WO$_4$)$_4$** | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 364 | 27473 | $^6H_{5/2} \rightarrow {}^4D_{3/2}$ |
| | 377 | 26525 | $^6H_{5/2} \rightarrow {}^6P_{7/2}$ |
| | 392 | 25510 | $^6H_{5/2} \rightarrow {}^4L_{15/2}$ |
| | 405 | 24691 | $^6H_{5/2} \rightarrow {}^4L_{13/2}$ |
| | 420 | 23810 | $^6H_{5/2} \rightarrow ({}^6P,{}^4P)_{5/2}$ |
| | 440 | 22727 | $^6H_{5/2} \rightarrow {}^4G_{9/2}$ |
| | 452 | 22124 | $^6H_{5/2} \rightarrow {}^4F_{5/2}$ |
| | 464 | 21552 | $^6H_{5/2} \rightarrow {}^6I_{13/2}$ |

| | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
|---|---|---|---|
| | 476 | 21008 | $^6H_{5/2} \rightarrow {}^4I_{11/2}$ |
| | 481 | 20790 | $^6H_{5/2} \rightarrow {}^4M_{15/2}$ |
| | 491 | 20367 | $^6H_{5/2} \rightarrow {}^4I_{9/2}$ |
| | 502 | 19920 | $^6H_{5/2} \rightarrow {}^4G_{7/2}$ |
| | 531 | 18832 | $^6H_{5/2} \rightarrow {}^4F_{3/2}$ |
| | 562 | 17794 | $^6H_{5/2} \rightarrow {}^4G_{5/2}$ |
| Na$_5$Eu(WO$_4$)$_4$ [b] | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 395 | 25316 | $^7F_0 \rightarrow {}^5L_6$ |
| | 465; 474 | 21505 | $^7F_0 \rightarrow {}^5D_2$ |
| | 526; 536 | 19011 | $^7F_0 \rightarrow {}^5D_1$ |
| | 579 | 17271 | $^7F_0 \rightarrow {}^5D_0$ |
| Na$_5$Dy(WO$_4$)$_4$ | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 327 | 30581 | $^6H_{15/2} \rightarrow {}^6P_{3/2}$ |
| | 353 | 28329 | $^6H_{15/2} \rightarrow {}^6P_{7/2}$ |
| | 366 | 27322 | $^6H_{15/2} \rightarrow {}^4M_{19/2}$ |
| | 388 | 25773 | $^6H_{15/2} \rightarrow {}^4I_{13/2}$ |
| | 428 | 23364 | $^6H_{15/2} \rightarrow {}^4G_{11/2}$ |
| | 454 | 22026 | $^6H_{15/2} \rightarrow {}^4I_{15/2}$ |
| | 475 | 21053 | $^6H_{15/2} \rightarrow {}^4F_{9/2}$ |
| | 759 | 13175 | $^6H_{15/2} \rightarrow {}^6F_{3/2}$ |
| Na$_5$Ho(WO$_4$)$_4$ | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 335 | 29851 | $^5I_8 \rightarrow ({}^3F, {}^3H, {}^3G)_4$ |
| | 347 | 28818 | $^5I_8 \rightarrow {}^5G_3$ |
| | 361 | 27701 | $^5I_8 \rightarrow ({}^5G, {}^3H)_5$ |
| | 383 | 26110 | $^5I_8 \rightarrow {}^3K_7$ |
| | 388 | 25773 | $^5I_8 \rightarrow {}^5G_4$ |
| | 419 | 23867 | $^5I_8 \rightarrow ({}^5G, {}^3G)_5$ |
| | 452 | 22124 | $^5I_8 \rightarrow {}^5F_1, {}^5G_6$ |
| | 469 | 21322 | $^5I_8 \rightarrow {}^3K_8$ |
| | 475 | 21053 | $^5I_8 \rightarrow {}^5F_2$ |
| | 480; 487 | 20833 | $^5I_8 \rightarrow {}^5F_3$ |
| | 540 | 18519 | $^5I_8 \rightarrow {}^5F_4, {}^5S_2$ |
| | 644; 654; 659 | 15528 | $^5I_8 \rightarrow {}^5F_5$ |
| Na$_5$Er(WO$_4$)$_4$ | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 357 | 28011 | $^4I_{15/2} \rightarrow {}^2G_{7/2}$ |
| | 366 | 27322 | $^4I_{15/2} \rightarrow {}^4G_{9/2}$ |

| | | | |
|---|---|---|---|
| | 379 | 26385 | $^4I_{15/2} \rightarrow {}^4G_{11/2}$ |
| | 407 | 24570 | $^4I_{15/2} \rightarrow (^2G, {}^4F)_{9/2}$ |
| | 445; 452 | 22472 | $^4I_{15/2} \rightarrow {}^4F_{5/2}$ |
| | 488 | 20492 | $^4I_{15/2} \rightarrow {}^4F_{7/2}$ |
| | 521 | 19194 | $^4I_{15/2} \rightarrow (^2H, {}^4G)_{11/2}$ |
| | 539; 545; 551 | 18553 | $^4I_{15/2} \rightarrow {}^4S_{3/2}$ |
| | 653 | 15314 | $^4I_{15/2} \rightarrow {}^4F_{9/2}$ |
| | 769 | 13004 | $^4I_{15/2} \rightarrow {}^4I_{9/2}$ |
| $Na_5Tm(WO_4)_4$ | Wavelength λ / nm | Energy E / cm$^{-1}$ | f-f transition |
| | 359 | 27855 | $^3H_6 \rightarrow {}^1D_2$ |
| | 466; 473 | 21459 | $^3H_6 \rightarrow {}^1G_4$ |
| | 662 | 15106 | $^3H_6 \rightarrow {}^3F_2$ |
| | 690; 704 | 14493 | $^3H_6 \rightarrow {}^3F_3$ |
| | 786; 795 | 12723 | $^3H_6 \rightarrow {}^3H_4$ |

[a] Doublets and triplets are marked by two or three values in the λ column. Only the respective energy for the first value is displayed. [b] The $O^{2-}$—$W^{6+}$ LMCT (λ = 230 nm) is overlapped with the $O^{2-}$—$Eu^{3+}$ LMCT (λ = 250nm).

**Table S13.** Assignment of emission and excitation peaks in the fluorescence spectra of Na$_5$$M$(WO$_4$)$_4$.[8,9,10,13,14,19,20,21,22,23,24,25,26,27,28] [a]

**Na$_5$Pr(WO$_4$)$_4$**

| Excitation | Wavelength λ / nm | Energy E / cm$^{-1}$ | Assignment |
|---|---|---|---|
| A | 250 | 40000 | O$^{2-}$–W$^{6+}$ LMCT |
| B | 446 | 22422 | $^3$H$_4$ → $^1$I$_6$ |
| C | 470 | 21277 | $^3$H$_4$ → $^3$P$_1$ |
| D | 484 | 20661 | $^3$H$_4$ → $^3$P$_0$ |

| Emission | Wavelength λ / nm | Energy E / cm$^{-1}$ | Assignment |
|---|---|---|---|
| | 481; 488, 496 | 20790 | $^3$P$_0$ → $^3$H$_4$ |
| | 528 | 18939 | $^3$P$_1$ → $^3$H$_5$ |
| | 546, 553 | 18315 | $^3$P$_0$ → $^3$H$_5$ |
| | 595 | 16807 | $^1$D$_2$ → $^3$H$_4$ |
| | 616 | 16234 | $^3$P$_0$ → $^3$H$_6$ |
| | 646 | 15480 | $^3$P$_0$ → $^3$F$_2$ |
| | 680 | 14706 | $^3$P$_0$ → $^3$F$_3$ |
| | 730 | 13699 | $^3$P$_0$ → $^3$F$_4$ |

**Na$_5$Sm(WO$_4$)$_4$**

| Excitation | Wavelength λ / nm | Energy E / cm$^{-1}$ | Assignment |
|---|---|---|---|
| A | 240 | 41667 | O$^{2-}$–W$^{6+}$ LMCT |
| B | 304 | 32895 | $^6$H$_{5/2}$ → $^4$P$_{5/2}$ |
| C | 316 | 31646 | $^6$H$_{5/2}$ → $^4$P$_{3/2}$ |
| D | 331 | 30211 | $^6$H$_{5/2}$ → $^4$G$_{9/2}$ |
| E | 344 | 29070 | $^6$H$_{5/2}$ → ($^4$H$_{9/2}$,$^4$D$_{7/2}$) |
| F | 362 | 27624 | $^6$H$_{5/2}$ → $^4$D$_{3/2}$ |
| G | 375 | 266667 | $^6$H$_{5/2}$ → $^6$P$_{7/2}$ |
| H | 390 | 25641 | $^6$H$_{5/2}$ → $^4$L$_{15/2}$ |
| I | 403 | 24814 | $^6$H$_{5/2}$ → $^4$L$_{13/2}$ |
| J | 417 | 23981 | $^6$H$_{5/2}$ → ($^6$P,$^4$P)$_{5/2}$ |
| K | 439 | 22779 | $^6$H$_{5/2}$ → $^4$G$_{9/2}$ |
| L | 448 | 22321 | $^6$H$_{5/2}$ → $^4$F$_{5/2}$ |
| M | 465 | 21505 | $^6$H$_{5/2}$ → $^6$I$_{13/2}$ |
| N | 471 | 21231 | $^6$H$_{5/2}$ → $^4$I$_{11/2}$ |
| O | 479 | 20877 | $^6$H$_{5/2}$ → $^4$M$_{15/2}$ |
| P | 487 | 20534 | $^6$H$_{5/2}$ → $^4$I$_{9/2}$ |
| Q | 497 | 20121 | $^6$H$_{5/2}$ → $^4$G$_{7/2}$ |

| Emission | Wavelength λ / nm | Energy E / cm$^{-1}$ | Assignment |
|---|---|---|---|

| | Wavelength λ / nm | Energy E / cm⁻¹ | Assignment |
|---|---|---|---|
| | 553; 562 | 17794 | $^4G_{5/2} \to {}^6H_{5/2}$ |
| | 600 | 16667 | $^4G_{5/2} \to {}^6H_{7/2}$ |
| | 645; 664 | 15504 | $^4G_{5/2} \to {}^6H_{9/2}$ |
| | 703 | 14225 | $^4G_{5/2} \to {}^6H_{11/2}$ |
| | 772 | 12953 | $^4G_{5/2} \to {}^6H_{13/2}$ |

**Na$_5$Eu(WO$_4$)$_4$**

| Excitation | Wavelength λ / nm | Energy E / cm⁻¹ | Assignment |
|---|---|---|---|
| A | 270 | 37037 | $O^{2-}$—$W^{6+}$ LMCT + $O^{2-}$-$Eu^{3+}$ LMCT |
| B | 285 | 35088 | $^7F_0 \to ({}^5I, {}^5H)_6$ |
| C | 293 | 34130 | $^7F_0 \to {}^5F_5$ |
| D | 298 | 33557 | $^7F_0 \to {}^5F_4$ |
| E | 302 | 33113 | $^7F_0 \to {}^5F_2$ |
| F | 305 | 32787 | $^7F_0 \to {}^3P_0$ |
| G | 317 | 31546 | $^7F_0 \to {}^5H_6$ |
| H | 321 | 31153 | $^7F_0 \to {}^5H_7$ |
| I | 326 | 30675 | $^7F_0 \to {}^5H_3$ |
| J | 361 | 27701 | $^7F_0 \to {}^5D_4$ |
| K | 366 | 27322 | $^7F_0 \to {}^5L_3$ |
| L | 375 | 26667 | $^7F_0 \to {}^5G_6$ |
| M | 380 | 26316 | $^7F_0 \to {}^5L_7$ |
| N | 383 | 26110 | $^7F_0 \to {}^5G_2$ |
| O | 393; 396; 399 | 25445 | $^7F_0 \to {}^5L_6$ |
| P | 415 | 24096 | $^7F_0 \to {}^5D_3$ |
| Q | 464; 472, 481, 488 | 21552 | $^7F_0 \to {}^5D_2$ |

| Emission | Wavelength λ / nm | Energy E / cm⁻¹ | Assignment |
|---|---|---|---|
| | 535 | 18692 | $^5D_0 \to {}^7F_0$ |
| | 591 | 16920 | $^5D_0 \to {}^7F_1$ |
| | 606; 611; 615 | 16502 | $^5D_0 \to {}^7F_2$ |
| | 653 | 15314 | $^5D_0 \to {}^7F_3$ |
| | 693; 699; 702 | 14430 | $^5D_0 \to {}^7F_4$ |

**Na$_5$Tb(WO$_4$)$_4$**

| Excitation | Wavelength λ / nm | Energy E / cm⁻¹ | Assignment |
|---|---|---|---|
| A | 251 | 39841 | $O^{2-}$—$W^{6+}$ LMCT + $Tb^{3+}$ 4f $\to$ 5d |
| B | 284 | 35211 | $^7F_6 \to {}^5I_8$ |
| C | 295 | 33898 | $^7F_6 \to {}^5H_5$ |
| D | 303 | 33003 | $^7F_6 \to {}^5H_6$ |

| | | | |
|---|---|---|---|
| E | 317 | 31546 | $^7F_6 \rightarrow {}^5H_7$ |
| F | 326 | 30675 | $^7F_6 \rightarrow {}^5D_1$ |
| G | 339 | 29499 | $^7F_6 \rightarrow {}^5L_7$ |
| H | 351 | 28490 | $^7F_6 \rightarrow {}^5L_9$ |
| I | 358 | 27933 | $^7F_6 \rightarrow {}^5G_5$ |
| J | 369 | 27100 | $^7F_6 \rightarrow {}^5L_{10}$ |
| K | 377 | 26525 | $^7F_6 \rightarrow {}^5G_6$ |
| Emission | Wavelength $\lambda$ / nm | Energy $E$ / cm$^{-1}$ | Assignment |
| | 487; 493 | 20534 | $^5D_4 \rightarrow {}^7F_6$ |
| | 543; 547 | 18416 | $^5D_4 \rightarrow {}^7F_5$ |
| | 581; 587 | 17212 | $^5D_4 \rightarrow {}^7F_4$ |
| | 616; 620 | 16234 | $^5D_4 \rightarrow {}^7F_3$ |
| | 644; 650 | 15528 | $^5D_4 \rightarrow {}^7F_2$ |
| | 669 | 14948 | $^5D_4 \rightarrow {}^7F_1$ |
| | 679 | 14728 | $^5D_4 \rightarrow {}^7F_0$ |
| $Na_5Bi(WO_4)_4$ [b] | | | |
| Excitation | Wavelength $\lambda$ / nm | Energy $E$ / cm$^{-1}$ | Assignment |
| | 250; 258 | 40000 | $O^{2-} \rightarrow W^{6+}$ LMCT |
| | 273; 275 | 36630 | $^1S_o \rightarrow {}^1P_1$ |
| | 281; 290 | 35587 | $^1S_o \rightarrow {}^3P_1$ |
| Emission | Wavelength $\lambda$ / nm | Energy $E$ / cm$^{-1}$ | Assignment |
| | 470 | 21277 | $^3P_1 \rightarrow {}^1S_0$ |

[a] Doublets, triplets et cetera are marked by two or three values in the $\lambda$ column. Only the respective energy for the first value is displayed. [b] The two $\lambda$ values for $Na_5Bi(WO_4)_4$ represent the maxima at both room temperature and 77 K.
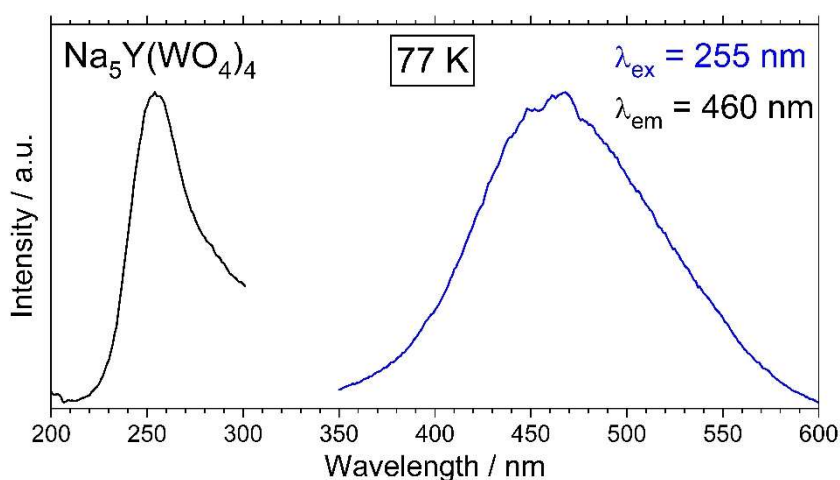


Fig. S20: Excitation and emission spectra of $Na_5Y(WO_4)_4$ measured at 77 K: the compound shows a broad $W^{6+}$-$O^{2-}$ LMCT emission centred at 460 nm; the excitation spectrum was not corrected with respect to the lamp intensity.
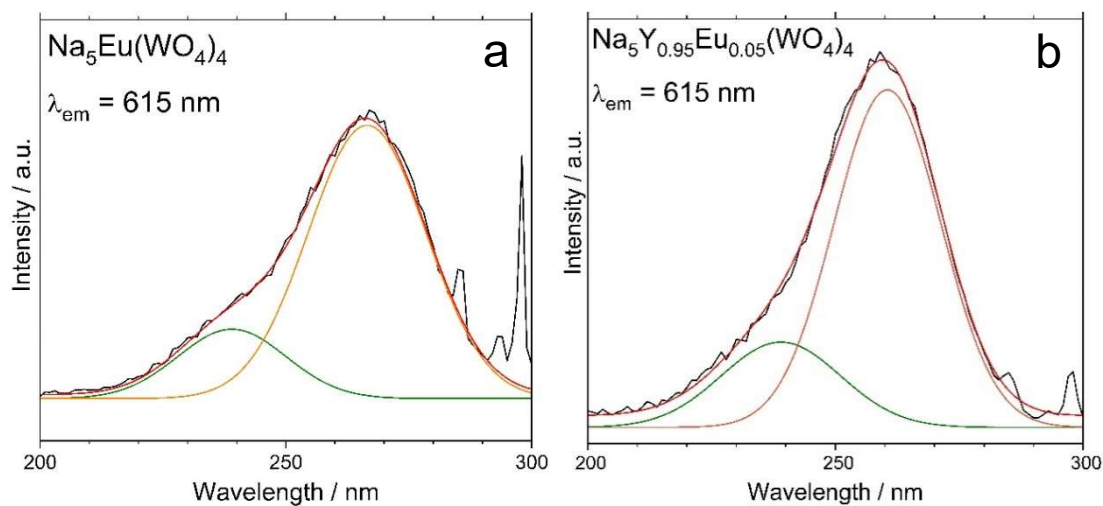
**Fig. S21: Gaussian fit of the excitation spectra of Na$_5$Eu(WO$_4$)$_4$ (a) and Na$_5$Y$_{0.95}$Eu$_{0.05}$(WO$_4$)$_4$ (b): they were fitted using two peaks centred at 239 nm (O$^{2-}$―W$^{6+}$ LMCT) for both spectra and at 266.5 nm (a) and 260.5 nm (b) (O$^{2-}$-Eu$^{3+}$ LMCT), respectively; the excitation spectra are corrected with respect to the lamp intensity.**
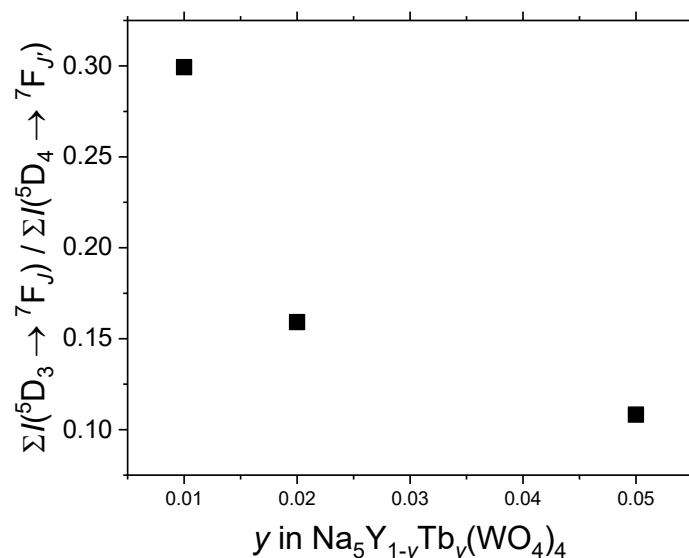


**Fig. S22: Trend of the ratio of the emission intensity related to the $^5D_4 \rightarrow {}^7F_5$ transitions and the $^5D_4 \rightarrow {}^7F_5$ transition of Tb$^{3+}$ varying with *y* in Na$_5$Y$_{1-y}$Tb$_y$(WO$_4$)$_4$.**
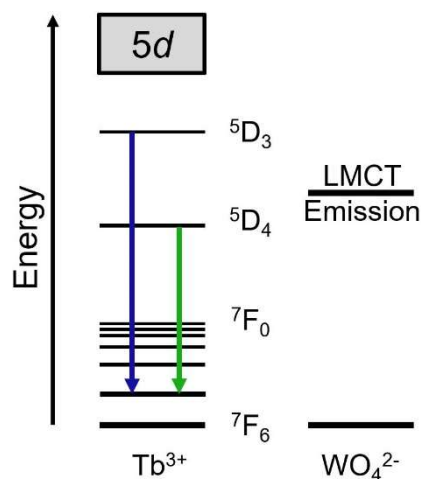
**Fig. S23: Energy Levels of the Tb$^{3+}$ f-states compared to the energy of the W$^{6+}$-O$^{2-}$ LMCT: The transferred energy is sufficient to reach the green emitting $^5D_4$ state, only. Consequently, no blue emission originating in the $^5D_3$ state is observed when exciting the WO$_4^{2-}$ ion's LMCT.**
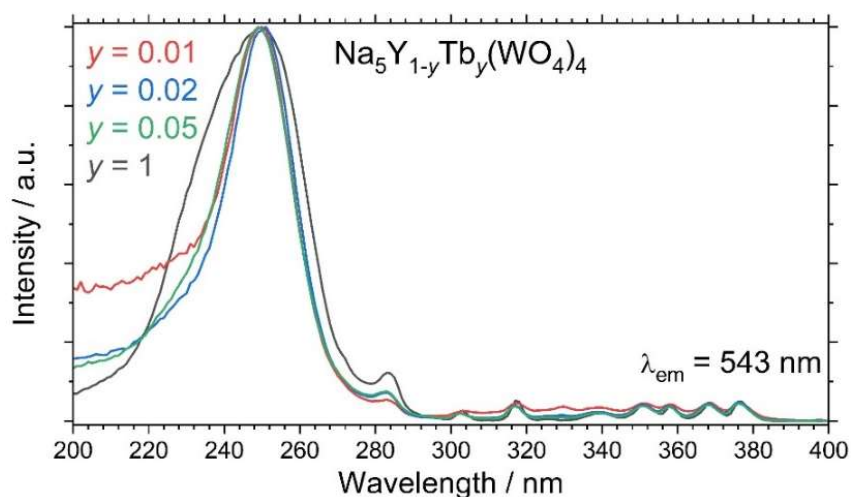


**Fig. S24: Excitation spectra of Na$_5$Y$_{1-y}$Tb$_y$(WO$_4$)$_4$ ($y$ = 0.01, 0.02, 0.05, 1) showing an increase of the intensity ratio of the broad LMCT band around 250 nm and the f-f transitions of Tb$^{3+}$ with decreasing Tb$^{3+}$ content.**
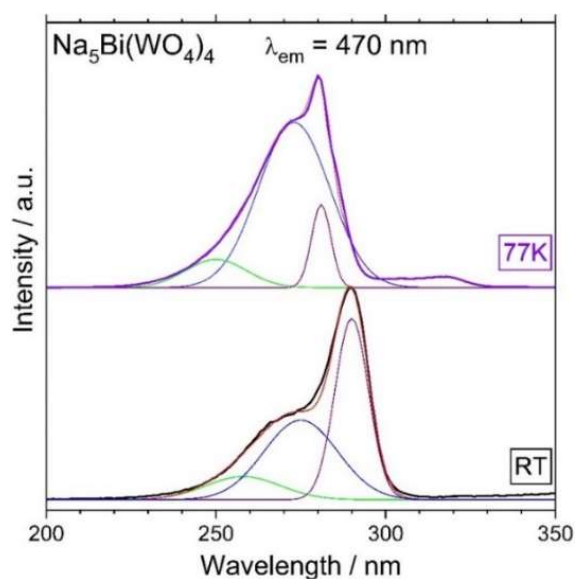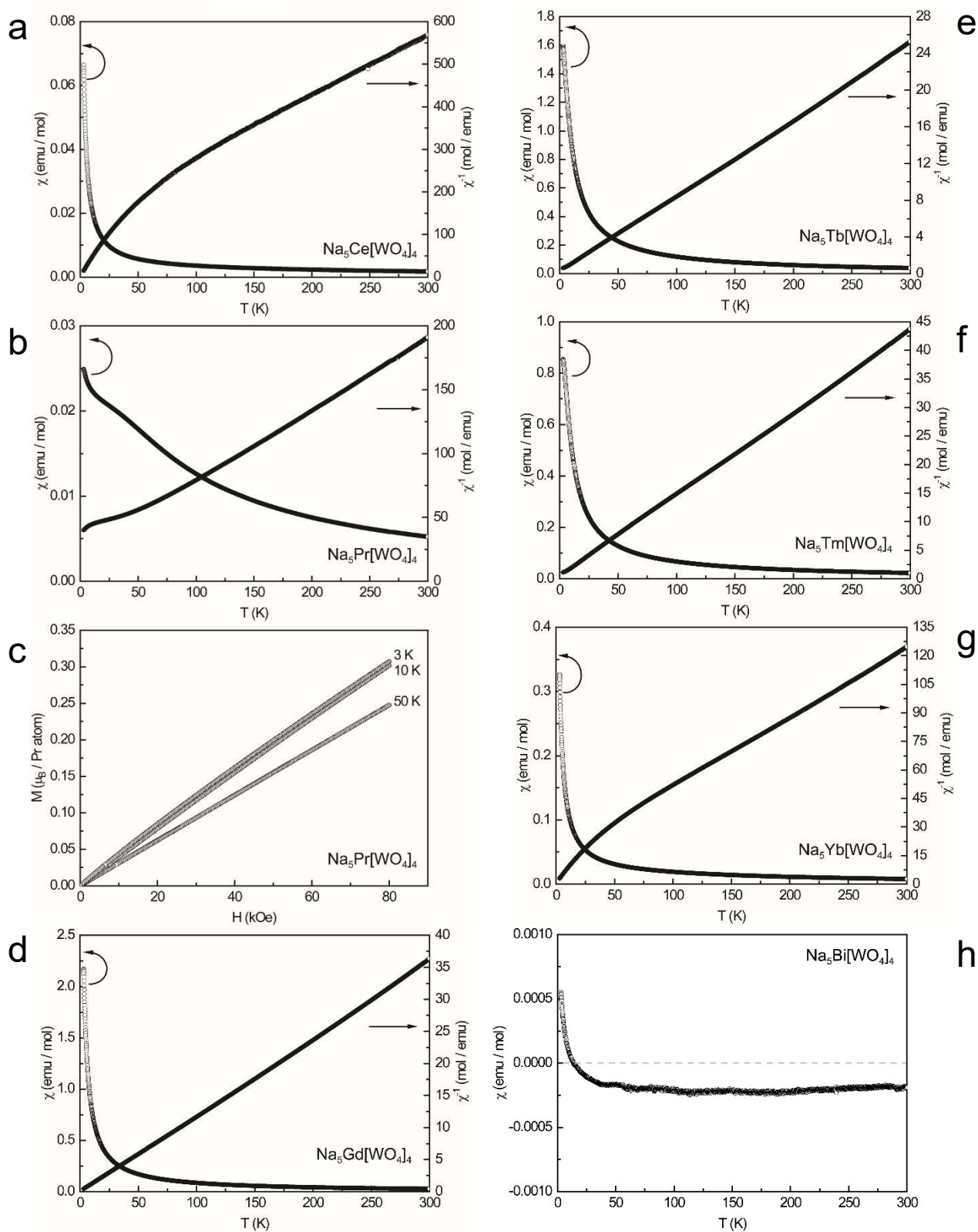


**Fig. S25: Gaussian fit of the excitation spectra of Na$_5$Bi(WO$_4$)$_4$ at both room temperature and 77K. The excitation spectra are not corrected with respect to the lamp intensity.**

**Fig. S26: Magnetic properties of Na$_5$$M$(WO$_4$)$_4$: temperature dependence of the magnetic susceptibility ($\chi$ and $\chi^{-1}$ data) measured at 10 kOe of magnetic properties of (a) Na$_5$Ce(WO$_4$)$_4$, (b) Na$_5$Pr(WO$_4$)$_4$, (d) Na$_5$Gd(WO$_4$)$_4$, (e) Na$_5$Tb(WO$_4$)$_4$, (f) Na$_5$Tm(WO$_4$)$_4$, (g) Na$_5$Yb(WO$_4$)$_4$ and (h) Na$_5$Bi(WO$_4$)$_4$; (c) magnetic properties of Na$_5$Pr(WO$_4$)$_4$: magnetisation isotherms at 3, 10 and 50 K.**

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