## *Supplementary material*

**Table 1.** Final coordinates, equivalent isotropic displacement parameters and Fourier amplitudes of the displacive modulation function in β-$K_5Yb(MoO_4)$. The modulation terms are given by s for sinus, c for cosinus and *n* for the order.

| | Wave | x | y | z | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|---|
| Yb | | 0 | 0 | 0 | 0.0144(4) |
| | s,1 | 0 | -0.00377(14) | 0 | |
| | c,1 | 0 | 0 | 0 | |
| | s,2 | 0 | 0.0044(2) | 0 | |
| | c,2 | 0 | 0 | 0 | |
| K1 | | 0 | 0 | 0 | 0.0144(4) |
| | s,1 | 0 | 0.0243(8) | 0 | |
| | c,1 | 0 | 0 | 0 | |
| | s,2 | 0 | 0.0128(10) | 0 | |
| | c,2 | 0 | 0 | 0 | |
| K2a | | 0.6167(3) | 0 | 0.21389(15) | 0.0319(14) |
| | s,1 | 0 | 0.0244(3) | 0 | |
| | c,1 | 0.0029(4) | 0 | -0.0009(2) | |
| | s,2 | 0 | -0.0022(4) | 0 | |
| | c,2 | -0.0086(4) | 0 | -0.0034(3) | |
| | s,3 | 0 | -0.0001(5) | 0 | |
| | c,3 | 0.0030(5) | 0 | -0.0005(3) | |
| K2b | | 0.5657(10) | 0 | 0.1801(6) | 0.0319(14) |
| | s,1 | 0 | -0.009(3) | 0 | |
| | c,1 | -0.003(3) | 0 | 0.0056(17) | |
| Mo | | 0.2118 | 0 | 0.4059 | 0.0143(5) |
| O1 | | 0.2338(6) | 0.2327(7) | 0.3658(3) | 0.028(3) |
| O2 | | 0.0048(8) | 0 | 0.3711(5) | 0.031(5) |
| O3 | | 0.3791(9) | 0 | 0.5260(4) | 0.030(5) |

**Table 2.** Starting values and Fourier amplitudes for the rotation and translation modulations of the two positions of the [MoO4] rigid unit in β-K5Yb(MoO4)4. See Table 1 for the signification of the terms.

| Position | Wave | Rotation components | | | Translation components | | |
|---|---|---|---|---|---|---|---|
| | | $r_x$ | $r_y$ | $r_z$ | $t_x$ | $t_y$ | $t_z$ |
| (a) | | 0 | 0 | 0 | -0.00030(11) | 0 | -0.00013(6) |
| | s,1 | 0 | 0.00152(9) | 0 | 0.0195(3) | 0 | -0.00378(16) |
| | c,1 | -0.00194(14) | 0 | -0.00270(7) | 0 | -0.0279(4) | 0 |
| | s,2 | 0 | 0.00379(14) | 0 | -0.0028(3) | 0 | -0.00075(17) |
| | c,2 | -0.00216(19) | 0 | 0.00164(11) | 0 | -0.0123(5) | 0 |
| | s,3 | 0 | -0.00138(15) | 0 | 0.0028(4) | 0 | -0.0004(2) |
| | c,3 | 0.0002(2) | 0 | 0.00439(12) | 0 | -0.0113(6) | 0 |
| (b) | | 0 | 35.8(5) | 180 | -0.0608(5) | 0 | -0.0275(3) |
| | s,1 | 0 | -0.0047(7) | 0 | -0.0331(15) | 0 | -0.0057(9) |
| | c,1 | 0.001(2) | 0 | 0.0017(11) | 0 | 0.004(3) | 0 |

**Table 3.** Parameters of the Crenel function for the cations and for two positions of the [$MoO_4$] rigid unit centre in β-$K_5Yb(MoO_4)_4$

| | $x_4^0$ | o(occupancy) |
|---|---|---|
| Yb | 0 | 0.5124(17) |
| K1 | 0.5 | 0.4876(17) |
| K2a | 0.5 | 0.8631(17) |
| K2b | 0 | 0.1369(17) |
| Mo (a) | 0 | 0.8631(17) |
| Mo (b) | 0.5 | 0.1369(17) |

**Table 4.** Final displacement parameters and ADP modulation functions in β-$K_5Yb(MoO_4)_4$.

| | Wave | $U^{11}$ | $U^{22}$ | $U^{133}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|---|
| Yb | | 0.0165(3) | 0.0131(3) | 0.0167(3) | 0 | 0.0130(3) | 0 |
| | s,1 | 0 | 0 | 0 | 0 | 0 | 0 |
| | c,1 | 0.0027(4) | 0.0030(5) | 0.0005(5) | 0 | 0.0009(4) | 0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| K1 | | 0.0165(3) | 0.0131(3) | 0.0167(3) | 0 | 0.0130(3) | 0 |
| | s,1 | 0 | 0 | 0 | 0 | 0 | 0 |
| | c,1 | 0.0023(18) | -0.006(2) | -0.008(2) | 0 | -0.0043(18) | 0 |
| K2a | | 0.0276(10) | 0.0377(11) | 0.0235(11) | 0 | 0.0164(9) | 0 |
| K2b | | 0.0276(10) | 0.0377(11) | 0.0235(11) | 0 | 0.0164(9) | 0 |
| Mo | | 0.0161(3) | 0.0148(3) | 0.0163(3) | 0 | 0.0132(3) | 0 |
| O1 | | 0.025(2) | 0.028(2) | 0.025(3) | -0.0009(17) | 0.016(2) | 0.0049(18) |
| O2 | | 0.025(3) | 0.040(3) | 0.029(4) | 0 | 0.020(3) | 0 |
| O3 | | 0.035(4) | 0.034(4) | 0.027(3) | 0 | 0.024(3) | 0 |

**Table 5.** Selected cation-oxygen distances (Å) and angles (°) in the [$MoO_4$] tetrahedra in β-$K_5Yb(MoO_4)_4$.

| | Average | Minimal | Maximal |
|---|---|---|---|
| Yb-O1(a) | 2.293(14) | 2.168(14) | 2.686(14) |
| Yb-O2(a) | 2.31(3) | 2.21(3) | 2.45(3) |
| Yb-O2(b) | 2.26(19) | 2.2(3) | 2.36(13) |
| K1-O1(a) | 2.990(17) | 2.461(18) | 3.13(2) |
| K1-O2(a) | 2.84(4) | 2.55(3) | 3.10(7) |
| K1-O1(b) | 2.67(3) | 2.48(3) | 2.96(3) |
| K1-O3(a) | 2.97(3) | 2.90(3) | 3.17(3) |
| K1-O3(a) | 3.45(4) | 2.80(8) | 3.88(4) |
| K2a-O1a | 2.89(3) | 2.53(3) | 3.19(2) |
| K2a-O1a | 3.27(4) | 2.92(4) | 3.61(4) |
| K2a-O1a | 3.15(3) | 2.83(3) | 3.41(3) |
| K2a-O2a | 2.839(15) | 2.539(18) | 3.136(15) |
| K2a-O2a | 3.294(15) | 2.843(18) | 3.682(17) |
| K2a-O3a | 2.60(3) | 2.49(4) | 2.75(3) |
| K2a-O1b | 3.30(6) | 2.61(5) | 3.98(5) |
| K2a-O1b | 2.86(6) | 2.53(6) | 3.27(4) |
| K2a-O3b | 2.61(18) | 2.6(3) | 2.64(13) |

| | | | |
|---|---|---|---|
| K2a-O3b | 3.32(4) | 2.63(4) | 3.97(3) |
| K2b-O1a | 2.91(7) | 2.84(9) | 3.09(6) |
| K2b-O1a | 3.13(8) | 3.05(5) | 3.36(6) |
| K2b-O2a | 2.78(6) | 2.76(9) | 2.82(4) |
| K2b-O2a | 2.88(2) | 2.81(2) | 2.924(18) |
| K2b-O1b | 3.29(13) | 2.64(9) | 3.54(10) |
| K2b-O2b | 2.96(8) | 2.82(6) | 3.04(12) |
| Mo(a)-tetrahedron | | | |
| Mo-O1 x2 | 1.78(2) | 1.73(3) | 1.83(3) |
| Mo-O2 | 1.77(3) | 1.74(3) | 1.87(4) |
| Mo-O3 | 1.72(2) | 1.684(19) | 1.77(7) |
| O1-Mo-O2 | 110.4(12) | 108.2(14) | 113.3(13) |
| O1-Moa-O3 | 108.2(11) | 107.8(10) | 109.2(11) |
| O1-Mo-O1 | 111.8(18) | 107.0(17) | 113.3(17) |
| O2-Mo-O3 | 107.5(11) | 106(2) | 107.9(10) |
| Mo(b)-tetrahedron | | | |
| Mo-O1 x2 | 1.77(6) | 1.72(9) | 1.85(3) |
| Mo-O2 | 1.72(16) | 1.72(13) | 1.72(11) |
| Mo-O3 | 1.68(11) | 1.63(16) | 1.76(8) |
| O1-Mob-O2 | 111(4) | 109(4) | 111(5) |
| O1-Mob-O3 | 109(5) | 108(6) | 110(5) |
| O1-Mob-O1 | 112(8) | 111(9) | 113(6) |
| O2-Mob-O3 | 106(8) | 105(6) | 106(10) |