Structural and spectroscopic insights into performance of the K3Tb(PO4)2 green phosphor

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Details of beamline measurements

For the studies at beamline (with synchrotron radiation) the $K_3Tb(PO_4)_2$ powder was pressed into copper cuvettes without adding any glue or other chemicals to the samples. The cuvettes were attached to the holder with a drop of silver varnish that located only under cuvette. A photo of part of the sample holder with attached cuvettes filled with $K_3Tb(PO_4)_2$ powder can be seen in Fig. S1.

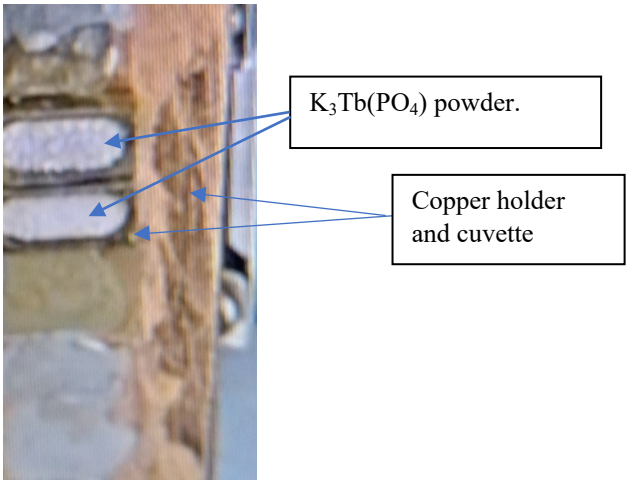

Fig. S1. Photo of the sample holder with cuvettes during measurements at SUPERLUMI station.

During the measurements of PL quantum yield on Horiba/Jobin-Yvon Fluorolog-3, the powder was poured into a special ceramic vessel made from non-luminescent material without any additional chemicals. A violet emission band was also observed during these measurements.

Comparison of the experimental and calculated powder XRD patterns

The phase purity of the bulk is confirmed by powder XRD analysis. Comparison of experimental and simulated patterns is given in Fig. S2. It is seen a good agreement between patterns with a moderate preferential orientation observed.

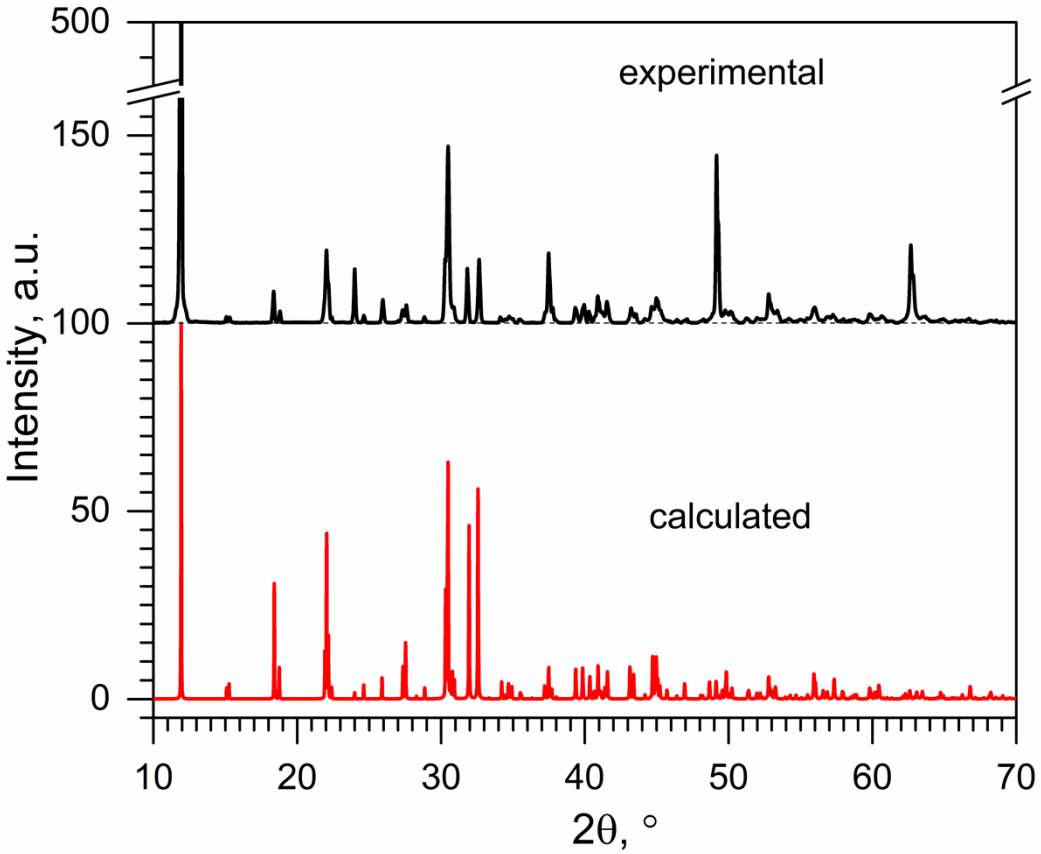

Fig. S2. Experimental and calculated powder XRD patterns of $K_3Tb(PO_4)_2$

SEM images and EDS analysis

Figure S3 shows the SEM images of the surface and deeper regions (backscattering electron, BSE) of the $K_3Tb(PO_4)_2$ crystals. Powdered sample consists mainly of grains with sizes about 0.5 μ those are tending to agglomeration. Some particles of size near 5 μ also can be found from BSE image on Figure S3a. The majority of the particles are relatively large, thus providing very small influence of surface defects on overall optical properties of the samples. The EDS analysis (Figure S3, parts b-e) has shown uniform distribution of K, Tb, P and O over the surface confirming a single-phase character of the sample. No traces of tungsten or any other impurity have been found from the EDS data.

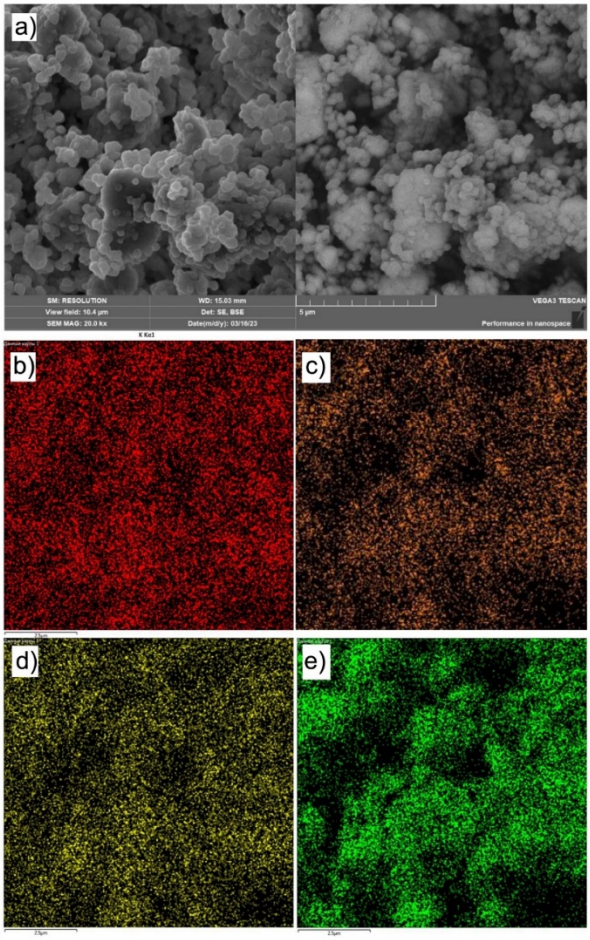

Fig. S3. SEM image of a $K_3Tb(PO_4)_2$ sample where EDS performed (a) and EDS mapping for K (b), Tb (c), P (d), and O (e).

Detailed view of diffuse reflectance spectrum

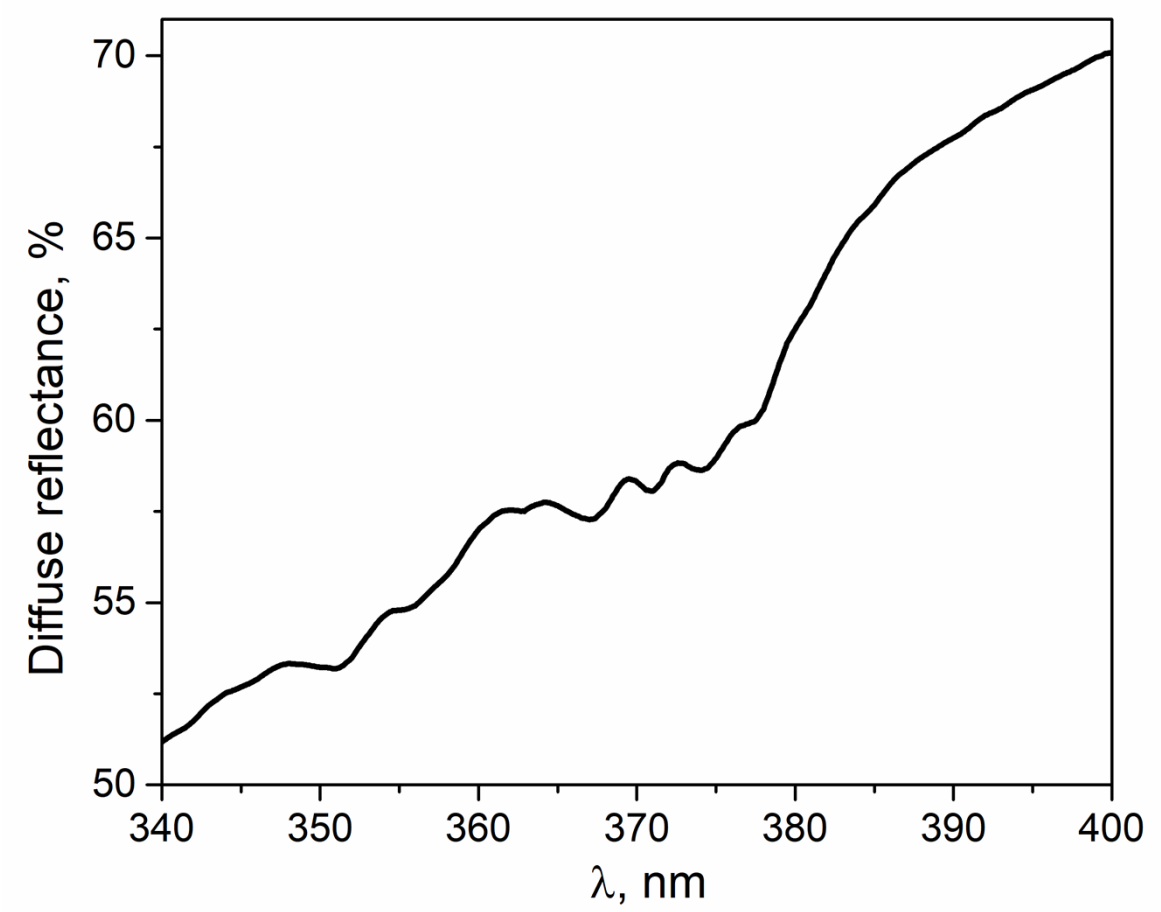

Fig. S4 Detailed view of diffuse reflectance spectrum of $K_3Tb(PO_4)_2$ at the region of slope

Photoluminescence quantum yield

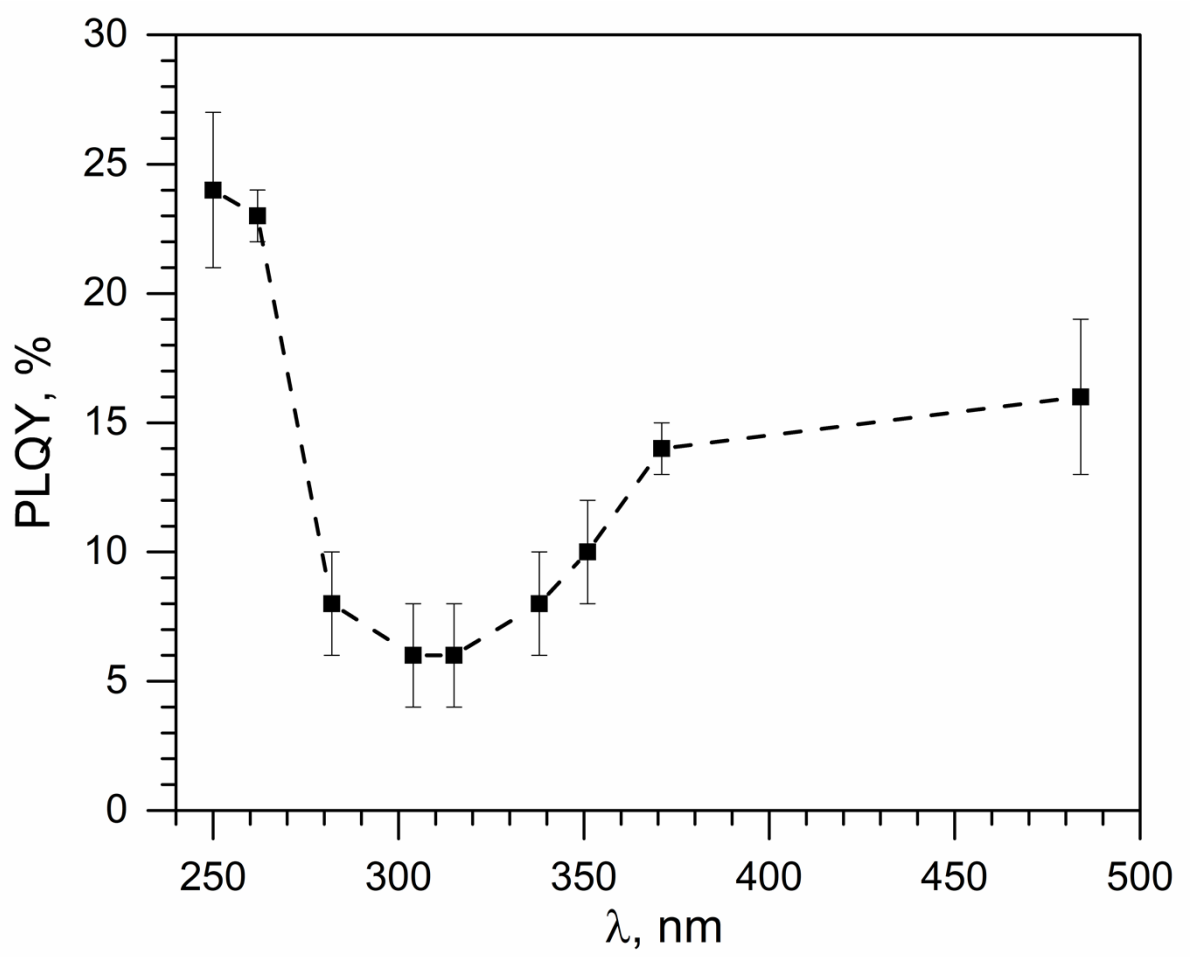

Fig. S5 Dependency of photoluminescence quantum yield of $K_3Tb(PO_4)_2$ on excitation wavelength. Dashed line is just guide for eyes. Vertical bars depict the standard deviations.

Table S1. Crystal data and structure refinement for $K_3Tb(PO_4)_2$

Empirical formula	$K_3O_8P_2Tb$
Formula weight	466.16
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	7.4128(18)
b/Å	5.5975(16)
c/Å	9.458(5)
α/°	90
β/°	90.65(3)
γ/°	90
Volume/Å^3	392.4(2)
Z	2
ρ_{calc}g/cm^3	3.945
μ/mm^{-1}	11.024
F(000)	432.0
Crystal size/mm^3	0.126 × 0.069 × 0.023
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.306 to 58.518
Index ranges	$-9 \leq h \leq 9$, $-6 \leq k \leq 7$, $-11 \leq l \leq 12$
Reflections collected	1879
Independent reflections	1879 [R_{sigma} = 0.0670]
Data/restraints/parameters	1879/6/80
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1100
Final R indexes [all data]	R_1 = 0.0604, wR_2 = 0.1128
Largest diff. peak/hole / e Å^{-3}	5.65/-2.46

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fizkarlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD- 2373835.

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $K_3Tb(PO_4)_2$

Atom	*x*	*y*	*z*	U(eq)
Tb1	-69.0(10)	2500	2114.0(9)	10.8(2)
K2	7951(4)	7500	4188(4)	14.4(7)
K1	3643(4)	-2500	897(4)	16.9(7)
K3	5037(5)	7500	6929(4)	16.9(7)
P1	-1900(5)	-2500	735(4)	8.0(8)
P2	2288(5)	7500	4114(5)	7.4(7)
O4	1514(11)	5256(13)	3366(8)	14.5(17)
O1	-2410(11)	-264(13)	1571(8)	14.5(17)
O6	1724(16)	7500	5676(11)	13(2)
O3	-2818(14)	-2500	-730(11)	14(2)
O2	145(14)	-2500	426(12)	16(2)
O5	4337(13)	7500	3980(12)	15(2)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $K_3Tb(PO_4)_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tb1	6.7(4)	11.7(4)	14.0(4)	0	0.5(2)	0
K2	15.2(17)	17.4(16)	10.6(16)	0	1.3(13)	0
K1	13.2(17)	20.7(17)	16.9(18)	0	1.1(14)	0
K3	13.5(16)	23.4(17)	13.7(19)	0	-2.6(13)	0
P1	7.3(18)	11.4(18)	5.3(19)	0	-1.1(15)	0
P2	7.5(18)	8.3(17)	6.4(18)	0	-0.3(14)	0
O4	20(4)	11(4)	12(4)	-3(3)	2(3)	-4(3)
O1	23(5)	11(4)	9(4)	-3(3)	-1(3)	-1(3)
O6	22(6)	7(5)	11(6)	0	-1(5)	0
O3	10(6)	22(6)	9(6)	0	0(4)	0
O2	13(6)	18(5)	18(6)	0	4(5)	0
O5	6(4)	21(4)	18(5)	0	2(4)	0

Table S4. Bond Lengths for $K_3Tb(PO_4)_2$.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tb1	K2[1]	3.728(2)		K1	O1[15]	2.938(8)
Tb1	K2[2]	3.817(4)		K1	O1[5]	2.938(8)
Tb1	K2[3]	3.728(2)		K1	O1[7]	3.239(8)
Tb1	K3[4]	3.802(4)		K1	O3[16]	2.869(3)
Tb1	P1[5]	3.079(4)		K1	O3[7]	3.057(11)
Tb1	O4[6]	2.264(7)		K1	O3[5]	2.869(3)
Tb1	O4	2.264(7)		K1	O2	2.626(11)
Tb1	O1[6]	2.377(7)		K1	O5[13]	2.955(12)
Tb1	O1	2.377(8)		K3	P2[2]	3.575(3)
Tb1	O6[4]	2.436(11)		K3	P2[8]	3.575(3)
Tb1	O3[5]	2.521(11)		K3	O4[2]	3.002(8)
Tb1	O2[5]	2.402(11)		K3	O4[9]	3.002(8)
K2	P2[7]	3.216(5)		K3	O1[4]	2.874(8)
K2	P2[8]	3.233(3)		K3	O1[17]	2.874(8)
K2	O4[9]	2.805(8)		K3	O6	2.715(12)
K2	O4[2]	2.805(8)		K3	O3[18]	2.711(11)
K2	O4[7]	3.034(8)		K3	O5[2]	2.966(4)
K2	O4[10]	3.034(8)		K3	O5[8]	2.966(4)
K2	O1[11]	2.784(8)		K3	O5	2.831(12)
K2	O1[12]	2.784(8)		P1	O1	1.530(8)
K2	O6[7]	3.116(12)		P1	O1[19]	1.530(8)
K2	O6[2]	2.8119(14)		P1	O3	1.537(11)
K2	O6[8]	2.8119(14)		P1	O2	1.547(11)
K2	O5	2.684(11)		P2	P2[20]	0.000(11)
K1	P2[13]	3.215(6)		P2	O4[20]	1.548(7)
K1	O4[6]	3.100(9)		P2	O4	1.548(7)
K1	O4[13]	3.100(9)		P2	O6	1.540(11)
K1	O1[14]	3.239(8)		P2	O5	1.526(11)

[1]-1+X,+Y,+Z; [2]1-X,1-Y,1-Z; [3]-1+X,-1+Y,+Z; [4]-X,1-Y,1-Z; [5]-X,-Y,-Z; [6]+X,1/2-Y,+Z; [7]1+X,+Y,+Z; [8]1-X,2-Y,1-Z; [9]1-X,1/2+Y,1-Z; [10]1+X,3/2-Y,+Z; [11]1+X,1/2-Y,+Z; [12]1+X,1+Y,+Z; [13]+X,-1+Y,+Z; [14]1+X,-1/2-Y,+Z; [15]-X,-1/2+Y,-Z; [16]-X,-1-Y,-Z; [17]-X,1/2+Y,1-Z; [18]1+X,1+Y,1+Z; [19]+X,-1/2-Y,+Z; [20]+X,3/2-Y,+Z

Table S5. Bond Angles for $K_3Tb(PO_4)_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
K2[1]	Tb1	K2[2]	97.30(8)	O6	K3	O4[3]	136.6(2)
K2[1]	Tb1	K2[3]	71.23(7)	O6	K3	O4[10]	136.6(2)
K2[2]	Tb1	K2[3]	71.23(7)	O6	K3	O1[17]	66.5(3)
K2[2]	Tb1	K3[4]	59.11(5)	O6	K3	O1[4]	66.5(3)
K2[1]	Tb1	K3[4]	59.11(5)	O6	K3	O5	54.2(3)
K3[4]	Tb1	K2[3]	99.86(8)	O6	K3	O5[8]	91.0(2)
P1[5]	Tb1	K2[2]	130.83(4)	O6	K3	O5[3]	91.0(2)
P1[5]	Tb1	K2[1]	130.83(4)	O3[18]	K3	K2	104.6(3)
P1[5]	Tb1	K2[3]	127.42(9)	O3[18]	K3	P2[8]	84.44(17)
P1[5]	Tb1	K3[4]	132.72(10)	O3[18]	K3	P2[3]	84.44(17)
O4	Tb1	K2[3]	46.8(2)	O3[18]	K3	O4[3]	65.4(3)
O4[6]	Tb1	K2[1]	116.2(2)	O3[18]	K3	O4[10]	65.4(3)
O4	Tb1	K2[2]	116.2(2)	O3[18]	K3	O1[17]	89.5(3)
O4	Tb1	K2[1]	54.4(2)	O3[18]	K3	O1[4]	89.5(3)
O4[6]	Tb1	K2[3]	46.8(2)	O3[18]	K3	O6	151.1(4)
O4[6]	Tb1	K2[2]	54.4(2)	O3[18]	K3	O5[8]	98.3(2)
O4[6]	Tb1	K3[4]	111.9(2)	O3[18]	K3	O5[3]	98.3(2)
O4	Tb1	K3[4]	111.9(2)	O3[18]	K3	O5	154.6(3)
O4[6]	Tb1	P1[5]	102.1(2)	O5[8]	K3	K2	71.1(2)
O4	Tb1	P1[5]	102.1(2)	O5[3]	K3	K2	71.1(2)
O4[6]	Tb1	O4	85.9(4)	O5	K3	K2	50.1(2)
O4	Tb1	O1[6]	92.4(3)	O5[8]	K3	P2[3]	124.7(2)
O4[6]	Tb1	O1[6]	158.3(3)	O5[3]	K3	P2[8]	124.7(2)
O4[6]	Tb1	O1	92.4(3)	O5[3]	K3	P2[3]	24.81(19)
O4	Tb1	O1	158.3(3)	O5	K3	P2[8]	79.88(16)
O4[6]	Tb1	O6[4]	79.3(3)	O5	K3	P2[3]	79.88(16)
O4	Tb1	O6[4]	79.3(3)	O5[8]	K3	P2[8]	24.81(19)
O4	Tb1	O3[5]	80.4(3)	O5[3]	K3	O4[3]	49.6(2)
O4[6]	Tb1	O3[5]	80.4(3)	O5	K3	O4[3]	93.2(2)
O4	Tb1	O2[5]	122.0(2)	O5[3]	K3	O4[10]	108.8(3)
O4[6]	Tb1	O2[5]	122.0(2)	O5[8]	K3	O4[3]	108.8(3)
O1[6]	Tb1	K2[2]	108.15(19)	O5	K3	O4[10]	93.2(2)
O1[6]	Tb1	K2[3]	119.31(19)	O5[8]	K3	O4[10]	49.6(2)
O1	Tb1	K2[1]	108.15(19)	O5	K3	O1[4]	111.6(2)
O1[6]	Tb1	K2[1]	48.25(19)	O5	K3	O1[17]	111.6(2)
O1	Tb1	K2[3]	119.31(19)	O5	K3	O5[8]	75.1(2)
O1	Tb1	K2[2]	48.25(19)	O5	K3	O5[3]	75.1(2)
O1	Tb1	K3[4]	49.06(19)	O5[3]	K3	O5[8]	141.4(4)
O1[6]	Tb1	K3[4]	49.06(19)	Tb1[5]	P1	K2[2]	153.65(15)
O1[6]	Tb1	P1[5]	99.4(2)	Tb1[5]	P1	K1[16]	77.69(9)
O1	Tb1	P1[5]	99.4(2)	Tb1[5]	P1	K1[5]	77.69(9)
O1	Tb1	O1[6]	81.2(4)	Tb1[5]	P1	K1[1]	121.60(15)
O1	Tb1	O6[4]	79.2(3)	K2[2]	P1	K1[16]	115.55(9)
O1[6]	Tb1	O6[4]	79.2(3)	K2[2]	P1	K1[5]	115.55(9)
O1[6]	Tb1	O3[5]	120.7(2)	K2[2]	P1	K1[1]	84.76(13)
O1	Tb1	O3[5]	120.7(2)	K1[1]	P1	K1[16]	69.56(9)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Tb1	O2^{5}	77.0(3)	K1^{16}	P1	K1^{5}	108.86(14)
O1^{6}	Tb1	O2^{5}	77.0(3)	K1^{1}	P1	K1^{5}	69.56(9)
O6^{4}	Tb1	K2^{2}	48.96(5)	O1	P1	Tb1^{5}	125.1(3)
O6^{4}	Tb1	K2^{1}	48.96(5)	O1^{19}	P1	Tb1^{5}	125.1(3)
O6^{4}	Tb1	K2^{3}	54.5(3)	O1	P1	K2^{2}	58.1(3)
O6^{4}	Tb1	K3^{4}	45.3(3)	O1^{19}	P1	K2^{2}	58.1(3)
O6^{4}	Tb1	P1^{5}	178.1(3)	O1^{19}	P1	K1^{5}	143.5(4)
O6^{4}	Tb1	O3^{5}	152.1(4)	O1	P1	K1^{5}	58.2(3)
O3^{5}	Tb1	K2^{2}	127.93(9)	O1^{19}	P1	K1^{16}	58.2(3)
O3^{5}	Tb1	K2^{3}	97.6(2)	O1	P1	K1^{16}	143.5(4)
O3^{5}	Tb1	K2^{1}	127.93(9)	O1^{19}	P1	K1^{1}	73.9(3)
O3^{5}	Tb1	K3^{4}	162.5(3)	O1	P1	K1^{1}	73.9(3)
O3^{5}	Tb1	P1^{5}	29.8(2)	O1^{19}	P1	O1	109.7(6)
O2^{5}	Tb1	K2^{1}	121.42(13)	O1^{19}	P1	O3	110.9(4)
O2^{5}	Tb1	K2^{2}	121.42(13)	O1	P1	O3	110.9(4)
O2^{5}	Tb1	K2^{3}	157.1(3)	O1	P1	O2	110.2(4)
O2^{5}	Tb1	K3^{4}	103.1(3)	O1^{19}	P1	O2	110.2(4)
O2^{5}	Tb1	P1^{5}	29.6(3)	O3	P1	Tb1^{5}	54.6(4)
O2^{5}	Tb1	O6^{4}	148.4(4)	O3	P1	K2^{2}	151.8(5)
O2^{5}	Tb1	O3^{5}	59.4(3)	O3	P1	K1^{5}	55.62(11)
P2^{7}	K2	P2^{8}	94.09(10)	O3	P1	K1^{16}	55.62(11)
O4^{9}	K2	P2^{7}	28.50(14)	O3	P1	K1^{1}	67.0(4)
O4^{3}	K2	P2^{8}	94.27(18)	O3	P1	O2	104.7(6)
O4^{7}	K2	P2^{7}	28.50(14)	O2	P1	Tb1^{5}	50.2(4)
O4^{7}	K2	P2^{8}	122.59(18)	O2	P1	K2^{2}	103.5(5)
O4^{10}	K2	P2^{8}	28.61(16)	O2	P1	K1^{1}	171.8(5)
O4^{10}	K2	P2^{7}	83.45(19)	O2	P1	K1^{5}	106.2(3)
O4^{3}	K2	P2^{7}	83.45(19)	O2	P1	K1^{16}	106.2(3)
O4^{9}	K2	P2^{8}	79.72(16)	K2^{1}	P2	K2^{8}	85.91(10)
O4^{10}	K2	O4^{3}	66.7(3)	K2^{8}	P2	K2^{3}	119.93(16)
O4^{9}	K2	O4^{7}	48.9(3)	K2^{1}	P2	K2^{3}	85.91(10)
O4^{3}	K2	O4^{7}	82.4(2)	K2^{1}	P2	K3^{8}	124.32(8)
O4^{10}	K2	O4^{9}	82.4(2)	K2^{3}	P2	K3^{3}	59.54(8)
O4^{3}	K2	O4^{9}	108.88(18)	K2^{8}	P2	K3^{3}	148.04(14)
O4^{10}	K2	O4^{7}	108.88(18)	K2^{8}	P2	K3^{8}	59.54(8)
O4^{10}	K2	O6^{8}	53.4(3)	K2^{1}	P2	K3^{3}	124.32(8)
O4^{3}	K2	O6^{8}	119.9(3)	K2^{3}	P2	K3^{8}	148.04(14)
O4^{10}	K2	O6^{7}	60.6(2)	K1^{20}	P2	K2^{3}	119.32(8)
O4^{9}	K2	O6^{7}	48.4(2)	K1^{20}	P2	K2^{1}	110.11(15)
O4^{3}	K2	O6^{3}	53.4(3)	K1^{20}	P2	K2^{8}	119.32(8)
O4^{10}	K2	O6^{3}	119.9(3)	K1^{20}	P2	K3^{8}	63.82(9)
O4^{3}	K2	O6^{7}	60.6(2)	K1^{20}	P2	K3^{3}	63.82(9)
O4^{7}	K2	O6^{7}	48.4(2)	K3^{8}	P2	K3^{3}	103.04(13)
O1^{11}	K2	P2^{7}	93.8(2)	P2^{21}	P2	K2^{8}	0(10)
O1^{11}	K2	P2^{8}	92.71(16)	P2^{21}	P2	K2^{3}	0(10)
O1^{12}	K2	P2^{8}	145.66(18)	P2^{21}	P2	K2^{1}	0(10)
O1^{12}	K2	P2^{7}	93.8(2)	P2^{21}	P2	K1^{20}	0(10)
O1^{12}	K2	O4^{10}	172.7(2)	P2^{21}	P2	K3^{3}	0(10)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[12]	K2	O4[7]	70.2(2)	P2[21]	P2	K3[8]	0(10)
O1[11]	K2	O4[7]	91.9(2)	P2[21]	P2	O4[21]	0(10)
O1[12]	K2	O4[9]	91.9(2)	P2[21]	P2	O4	0(10)
O1[11]	K2	O4[9]	70.2(2)	P2[21]	P2	O6	0(10)
O1[12]	K2	O4[3]	119.8(2)	P2[21]	P2	O5	0(10)
O1[11]	K2	O4[10]	119.8(2)	O4[21]	P2	K2[1]	69.2(3)
O1[11]	K2	O4[3]	172.7(2)	O4	P2	K2[3]	60.1(3)
O1[12]	K2	O1[11]	53.4(3)	O4	P2	K2[8]	155.1(4)
O1[12]	K2	O6[3]	66.5(3)	O4	P2	K2[1]	69.2(3)
O1[12]	K2	O6[7]	118.6(3)	O4[21]	P2	K2[8]	60.1(3)
O1[12]	K2	O6[8]	119.7(3)	O4[21]	P2	K2[3]	155.1(4)
O1[11]	K2	O6[3]	119.7(3)	O4[21]	P2	K1[20]	71.7(3)
O1[11]	K2	O6[8]	66.5(3)	O4	P2	K1[20]	71.7(3)
O1[11]	K2	O6[7]	118.6(3)	O4	P2	K3[3]	56.1(3)
O6[8]	K2	P2[7]	85.2(2)	O4[21]	P2	K3[3]	135.5(4)
O6[3]	K2	P2[7]	85.2(2)	O4	P2	K3[8]	135.5(4)
O6[7]	K2	P2[7]	28.1(2)	O4[21]	P2	K3[8]	56.1(3)
O6[3]	K2	P2[8]	147.6(3)	O4	P2	O4[21]	108.5(6)
O6[7]	K2	P2[8]	80.19(13)	O6	P2	K2[8]	60.42(9)
O6[8]	K2	P2[8]	28.4(2)	O6	P2	K2[3]	60.42(9)
O6[8]	K2	O4[7]	110.5(3)	O6	P2	K2[1]	72.3(5)
O6[3]	K2	O4[7]	61.6(3)	O6	P2	K1[20]	177.5(5)
O6[3]	K2	O4[9]	110.5(3)	O6	P2	K3[3]	115.0(2)
O6[8]	K2	O4[9]	61.6(3)	O6	P2	K3[8]	115.0(2)
O6[8]	K2	O6[7]	84.4(2)	O6	P2	O4	109.5(4)
O6[3]	K2	O6[7]	84.4(2)	O6	P2	O4[21]	109.5(4)
O6[8]	K2	O6[3]	168.9(5)	O5	P2	K2[3]	95.8(2)
O5	K2	P2[7]	174.5(3)	O5	P2	K2[1]	176.5(5)
O5	K2	P2[8]	88.64(16)	O5	P2	K2[8]	95.8(2)
O5	K2	O4[9]	148.5(2)	O5	P2	K1[20]	66.4(5)
O5	K2	O4[3]	101.1(3)	O5	P2	K3[3]	54.63(14)
O5	K2	O4[7]	148.5(2)	O5	P2	K3[8]	54.63(14)
O5	K2	O4[10]	101.1(3)	O5	P2	O4	109.0(4)
O5	K2	O1[11]	81.3(3)	O5	P2	O4[21]	109.0(4)
O5	K2	O1[12]	81.3(3)	O5	P2	O6	111.2(6)
O5	K2	O6[7]	157.4(4)	Tb1	O4	K2[3]	97.1(3)
O5	K2	O6[8]	95.1(2)	Tb1	O4	K2[1]	88.2(2)
O5	K2	O6[3]	95.1(2)	Tb1	O4	K1[20]	98.5(3)
P2[13]	K1	O1[7]	96.02(17)	Tb1	O4	K3[3]	92.2(2)
P2[13]	K1	O1[14]	96.02(17)	K2[3]	O4	K2[1]	97.6(2)
O4[6]	K1	P2[13]	28.32(14)	K2[3]	O4	K1[20]	140.9(3)
O4[13]	K1	P2[13]	28.32(14)	K2[1]	O4	K1[20]	118.5(3)
O4[6]	K1	O4[13]	47.8(3)	K2[3]	O4	K3[3]	71.4(2)
O4[6]	K1	O1[14]	118.3(2)	K3[3]	O4	K2[1]	169.0(3)
O4[13]	K1	O1[14]	99.3(2)	K3[3]	O4	K1[20]	72.34(19)
O4[13]	K1	O1[7]	118.3(2)	P2[21]	O4	Tb1	168.1(5)
O4[6]	K1	O1[7]	99.3(2)	P2	O4	Tb1	168.1(5)
O1[15]	K1	P2[13]	130.86(18)	P2	O4	K2[1]	82.3(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1^{5}	K1	P2^{13}	130.86(18)	P2^{21}	O4	K2^{3}	91.2(4)
O1^{15}	K1	O4^{6}	131.0(2)	P2	O4	K2^{3}	91.2(4)
O1^{5}	K1	O4^{13}	131.0(2)	P2^{21}	O4	K2^{1}	82.3(3)
O1^{5}	K1	O4^{6}	103.2(2)	P2	O4	K1^{20}	80.0(3)
O1^{15}	K1	O4^{13}	103.2(2)	P2^{21}	O4	K1^{20}	80.0(3)
O1^{15}	K1	O1^{7}	129.21(16)	P2	O4	K3^{3}	98.5(4)
O1^{5}	K1	O1^{14}	129.21(16)	P2^{21}	O4	K3^{3}	98.5(4)
O1^{15}	K1	O1^{14}	103.01(19)	P2^{21}	O4	P2	0.0(3)
O1^{15}	K1	O1^{5}	63.6(3)	Tb1	O1	K2^{2}	92.2(2)
O1^{7}	K1	O1^{14}	45.5(3)	Tb1	O1	K1^{1}	161.8(3)
O1^{5}	K1	O1^{7}	103.01(19)	Tb1	O1	K1^{5}	92.8(2)
O1^{15}	K1	O3^{7}	82.0(2)	Tb1	O1	K3^{4}	92.3(2)
O1^{5}	K1	O3^{7}	82.0(2)	K2^{2}	O1	K1^{1}	94.5(2)
O1^{15}	K1	O5^{13}	146.43(16)	K2^{2}	O1	K1^{5}	165.7(3)
O1^{5}	K1	O5^{13}	146.43(16)	K2^{2}	O1	K3^{4}	82.1(2)
O3^{7}	K1	P2^{13}	139.1(2)	K1^{5}	O1	K1^{1}	76.99(19)
O3^{5}	K1	P2^{13}	89.0(2)	K3^{4}	O1	K1^{1}	71.92(19)
O3^{16}	K1	P2^{13}	89.0(2)	K3^{4}	O1	K1^{5}	84.4(2)
O3^{7}	K1	O4^{13}	145.8(2)	P1	O1	Tb1	117.4(4)
O3^{5}	K1	O4^{6}	62.4(3)	P1	O1	K2^{2}	94.0(4)
O3^{5}	K1	O4^{13}	109.1(3)	P1	O1	K1^{1}	79.1(3)
O3^{7}	K1	O4^{6}	145.8(2)	P1	O1	K1^{5}	95.5(4)
O3^{16}	K1	O4^{13}	62.4(3)	P1	O1	K3^{4}	150.2(5)
O3^{16}	K1	O4^{6}	109.1(3)	Tb1^{4}	O6	K2^{8}	90.3(2)
O3^{16}	K1	O1^{7}	125.4(3)	Tb1^{4}	O6	K2^{3}	90.3(2)
O3^{5}	K1	O1^{15}	114.0(3)	Tb1^{4}	O6	K2^{1}	86.0(3)
O3^{16}	K1	O1^{5}	114.0(3)	Tb1^{4}	O6	K3	95.0(4)
O3^{7}	K1	O1^{14}	47.2(2)	K2^{8}	O6	K2^{1}	95.6(2)
O3^{5}	K1	O1^{14}	125.4(3)	K2^{8}	O6	K2^{3}	168.9(5)
O3^{5}	K1	O1^{5}	51.6(3)	K2^{3}	O6	K2^{1}	95.6(2)
O3^{7}	K1	O1^{7}	47.2(2)	K3	O6	K2^{1}	179.0(4)
O3^{16}	K1	O1^{15}	51.6(3)	K3	O6	K2^{8}	84.5(2)
O3^{16}	K1	O1^{14}	79.9(2)	K3	O6	K2^{3}	84.5(2)
O3^{5}	K1	O1^{7}	79.9(2)	P2	O6	Tb1^{4}	165.5(7)
O3^{16}	K1	O3^{7}	99.0(2)	P2^{21}	O6	Tb1^{4}	165.5(7)
O3^{16}	K1	O3^{5}	154.7(4)	P2^{21}	O6	K2^{8}	91.1(2)
O3^{5}	K1	O3^{7}	99.0(2)	P2	O6	K2^{1}	79.6(4)
O3^{5}	K1	O5^{13}	95.1(2)	P2	O6	K2^{3}	91.1(2)
O3^{16}	K1	O5^{13}	95.1(2)	P2^{21}	O6	K2^{3}	91.1(2)
O2	K1	P2^{13}	80.9(3)	P2	O6	K2^{8}	91.1(2)
O2	K1	O4^{6}	67.5(3)	P2^{21}	O6	K2^{1}	79.6(4)
O2	K1	O4^{13}	67.5(3)	P2^{21}	O6	K3	99.5(6)
O2	K1	O1^{7}	157.14(14)	P2	O6	K3	99.5(6)
O2	K1	O1^{5}	64.4(3)	P2^{21}	O6	P2	0.0(3)
O2	K1	O1^{15}	64.4(3)	Tb1^{5}	O3	K1^{16}	98.8(2)
O2	K1	O1^{14}	157.14(14)	Tb1^{5}	O3	K1^{1}	179.0(4)
O2	K1	O3^{16}	77.4(2)	Tb1^{5}	O3	K1^{5}	98.8(2)
O2	K1	O3^{7}	140.0(3)	Tb1^{5}	O3	K3^{22}	94.0(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	K1	O3^{5}	77.4(2)	K1^{5}	O3	K1^{1}	81.0(2)
O2	K1	O5^{13}	109.2(3)	K1^{16}	O3	K1^{1}	81.0(2)
O5^{13}	K1	P2^{13}	28.2(2)	K1^{16}	O3	K1^{5}	154.7(4)
O5^{13}	K1	O4^{13}	48.8(2)	K3^{22}	O3	K1^{1}	85.0(3)
O5^{13}	K1	O4^{6}	48.8(2)	K3^{22}	O3	K1^{16}	80.4(2)
O5^{13}	K1	O1^{14}	70.1(2)	K3^{22}	O3	K1^{5}	80.4(2)
O5^{13}	K1	O1^{7}	70.1(2)	P1	O3	Tb1^{5}	95.6(5)
O5^{13}	K1	O3^{7}	110.9(3)	P1	O3	K1^{16}	98.1(2)
K2	K3	P2^{3}	55.21(8)	P1	O3	K1^{1}	85.4(5)
K2	K3	P2^{8}	55.21(8)	P1	O3	K1^{5}	98.1(2)
P2^{8}	K3	P2^{3}	103.04(13)	P1	O3	K3^{22}	170.4(7)
O4^{10}	K3	K2	51.58(17)	Tb1^{5}	O2	K1	100.5(4)
O4^{3}	K3	K2	51.58(17)	P1	O2	Tb1^{5}	100.2(5)
O4^{3}	K3	P2^{8}	84.31(17)	P1	O2	K1	159.3(7)
O4^{10}	K3	P2^{3}	84.31(17)	K2	O5	K1^{20}	103.6(4)
O4^{10}	K3	P2^{8}	25.36(15)	K2	O5	K3	75.9(3)
O4^{3}	K3	P2^{3}	25.36(15)	K2	O5	K3^{8}	82.1(2)
O4^{10}	K3	O4^{3}	61.8(3)	K2	O5	K3^{3}	82.1(2)
O1^{4}	K3	K2	144.87(17)	K1^{20}	O5	K3^{8}	74.9(2)
O1^{17}	K3	K2	144.87(16)	K1^{20}	O5	K3^{3}	74.9(2)
O1^{4}	K3	P2^{3}	159.81(18)	K3	O5	K1^{20}	179.5(4)
O1^{17}	K3	P2^{8}	159.81(18)	K3^{3}	O5	K3^{8}	141.4(4)
O1^{4}	K3	P2^{8}	95.49(16)	K3	O5	K3^{8}	104.9(2)
O1^{17}	K3	P2^{3}	95.49(16)	K3	O5	K3^{3}	104.9(2)
O1^{4}	K3	O4^{3}	154.8(2)	P2	O5	K2	171.0(7)
O1^{4}	K3	O4^{10}	110.6(2)	P2^{21}	O5	K2	171.0(7)
O1^{17}	K3	O4^{3}	110.6(2)	P2	O5	K1^{20}	85.4(5)
O1^{17}	K3	O4^{10}	154.8(2)	P2^{21}	O5	K1^{20}	85.4(5)
O1^{17}	K3	O1^{4}	65.1(3)	P2	O5	K3^{3}	100.6(2)
O1^{4}	K3	O5^{8}	75.2(2)	P2^{21}	O5	K3	95.1(5)
O1^{17}	K3	O5^{8}	139.5(3)	P2	O5	K3	95.1(5)
O1^{17}	K3	O5^{3}	75.2(2)	P2^{21}	O5	K3^{3}	100.6(2)
O1^{4}	K3	O5^{3}	139.5(3)	P2^{21}	O5	K3^{8}	100.6(2)
O6	K3	K2	104.3(3)	P2	O5	K3^{8}	100.6(2)
O6	K3	P2^{8}	112.43(15)	P2^{21}	O5	P2	0.0(3)
O6	K3	P2^{3}	112.43(15)				

Table S6. Parameters of oxygen polyhedra in $K_3Tb(PO_4)_2$.

Moieties (MO_x)	**TbO_7**	**$K^{(2)}O_{10}$**	**$K^{(1)}O_9$**	**$K^{(3)}O_9$**	**$P^{(1)}O_4$**	**$P^{(2)}O_4$**
distances d_{M-O}, Å	2.2644 x2 2.3767 x2 2.4024 2.4356 2.5213	2.6840 2.7838 x2 2.8050 x2 2.8119 x2 3.0339 x2 3.1167	2.6260 2.8688 x2 2.9376 x2 2.9552 3.0564 3.0992 x2	2.7112 2.7147 2.8312 2.8742 x2 2.9659 x2 3.0017 x2	1.5302 1.5302 1.5367 1.5471	1.5256 1.5399 1.5486 1.5486
M site symmetry	*Cs*					
Polyhedron type	Caped trigonal prism	Sphenocorona J87	Muffin		Tetrahedron	
Symmetry of ideal polyhedron	C_{2v}		C_s		T_d	
S	0.690	7.987	8.048	5.372	0.056	0.007

Table S7. The positions (λ, nm) of the lines caused by electronic absorption transitions (numbered as ##1, 2, 3, …) from ground $^7F_6$ level on excited levels of the Tb^{3+} ions and energy of these transitions (ν in cm^{-1}, hν in eV) found from diffuse reflectance (λ_{DR}) and the PL excitation spectra (λ_{ex}) of the $K_3Tb(PO_4)_2$ crystals; *sh* – shoulder, *l* – low intensity

λ_{DR}	λ_{ex}	ν_{ex}	$h\nu_{ex}$, eV	Excited levels**	Transitions types	Transition, # in Fig. 10
	114	87758	10.88	$3t_2$	$2t_2 \rightarrow 3t_2$	1
	127	79531	9.86			2
	162	61624	7.64	2a	$2t_2 \rightarrow 2a$	3
	171	58479	7.25			4
	186.1	53735	6.66			5
	195.6	51125	6.34		spin-allowed	6
	210 (*sh*)	47619	5.90		$4f^8 \rightarrow 4f^7 5d^1$	
	215.5	46403	5.72	$4f^7 5d^1$		7
	223 (*sh*)	44843	5.56			
	225 (*sh*)	44444	5.51			8
258.5	253	39526	4.90		spin-forbidden	9
269.1	264	37879	4.70	$4f^7 5d^1$	$4f^8 \rightarrow 4f^7 5d^1$	10
	281	35587	4.41	$^5F_4$		11
	284 (*sh*)	35211	4.37			
	292 (*l*)	34247	4.25	$^5H_4$		
	300	33333	4.13			12
	305 (*sh*)	32787	4.06			
	314	31847	3.95			13
	318 (*sh*)	31447	3.90	$^5H_7$		
	325 (*l*)	30769	3.81			
	332 (*sh*)	30120	3.73			
	336	29762	3.69	$^5G_2$		14
	339 (*sh*)	29499	3.66			
	344 (*sh*)	29070	3.60		intrinsic	
	349 (*sh*)	28653	3.55	$^5L_9$	$4f^8 \rightarrow 4f^8$	
351	350	28571	3.54			15
356	355	28169	3.49	$^5D_2$		16
363	361 (*sh*)	27701	3.43			
367	366	27322	3.39			
371	369	27100	3.36			
374	373	26810	3.32	$^5D_3$		17
378	376	26596	3.30			
	398 (*l*)	25126	3.12			
	479 (*sh*)	20877	2.59			
483	482	20747	2.57	$^5D_4$		
488	486	20576	2.55			18
495	494	20243	2.51			

** [1, 2]

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