Green Light: On YCl[WO_4] as Host Material for Luminescence Active Tb^{3+} Cations

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Dedicated to Professor Wolfgang Bensch on the Occasion of his 65th Birthday

Abstract. Coarse, colorless and transparent single crystals as well as single phase powder of YCl[WO_4] were yielded by the reaction of Y_2O_3, YCl_3, and WO_3 in evacuated silica ampules at 850 °C for six days, utilizing a fivefold excess of YCl_3 with respect to the stoichiometric ratio as flux. The title compound crystallizes isotypically to the *RE*Cl[WO_4] representatives for *RE* = Gd – Tm in the monoclinic space group $C2/m$ (a = 1022.41(3), b = 722.91(2), c = 684.34(2) pm; β = 107.455(3)°; Z = 4). By doping the title compound with about 1 % Tb^{3+} cations, bright green luminescence is observed upon irradiation with UV light. Investigations of the excitation and emission spectra at room temperature as well as 77 K reveal a slight shift in the $O^{2-} \rightarrow W^{6+}$ LMCT transition towards shorter wavelengths upon reducing the temperature. This charge transfer transition can be used as sensitizer for the Tb^{3+} luminescence, however, the $^5D_3$ state of the latter is not reached by this excitation. This is possible by exciting the $^7F_6 \rightarrow {}^5G_6$ transition, which causes the emissions from the aforementioned $^5D_3$ level to intensify, thus causing a blue shift of the emission.

Introduction

The sensitizer ability of $[WO_4]^{2-}$ groups due to their ligand-to metal charge transfer (LMCT)[1] has long been known and also found wide application.[2] Tungstates of the luminescence-active rare-earth metals, such as $Eu_2W_3O_{12}$[3] were subject to thorough investigations as well as materials with RE^{3+} doping (e.g. Ca[WO_4]:Tb^{3+}).[4,5] Halide derivatives of trivalent rare-earth metal oxidomolybdates(VI) and -tungstates(VI) have also proven to be suitable host materials for luminescence applications due to the aforementioned sensitizer-activator interaction,[6–17] although in case of compounds comprising tetrahedral molybdate units the chloride derivatives appear to suffer from complete luminescence quenching, i.e. no luminescence upon appropriate UV excitation is detected.[12] For the longest known composition, $RE_3Cl_3[WO_6]$ (*RE* = rare-earth metal), bearing trigonal prismatic $[WO_6]^{6-}$ anions, both doped lanthanum and gadolinium compounds were subject to thorough investigations[6,17] regarding their abilities to host luminescence active cations, however, the isotypic yttrium compound has not been synthesized so far.

In case of the composition *RE*ClWO_4 several different structure types with condensed and isolated oxidotungstate entities are known. The structure of the largest cations comprises chains of apically vertex-sharing trigonal [WO_5] bipyramids and the lanthanum representative was also successfully investigated as host material.[7,10] GdCl[WO_4], which crystallizes isotypically to the title compound, and LuCl[WO_4] both are also ideally equipped to act as luminescence host and investigations on Eu^{3+}-doped derivatives show bright red luminescence as expected.[8,11,15] Unlike the also isotypic YCl[MoO_4][7] the yttrium chloride oxidotungstate YCl[WO_4] does not suffer from complete luminescence quenching upon doping with active cations as described in this contribution, since green luminescence is clearly visible in the Tb^{3+}-doped material when irradiated with UV light (see Figure 3).

Results and Discussion

Crystal Structure

YCl[WO_4] crystallizes in the monoclinic space group $C2/m$ (a = 1022.41(3), b = 722.91(2), c = 684.34(2) pm; β = 107.455(3)°) with four formula units per unit cell, thus isotypic to the *RE*Cl[WO_4] derivatives with (*RE* = Gd – Er)[15] as well as to YCl[MoO_4][12] and the *RE*Cl[MoO_4] representatives with (*RE* = Sm – Yb).[18] The crystal structure comprises crystallographically unique trivalent yttrium cations with a coordination number of eight, built up by two chloride and six oxide anions in the shape of distorted trigonal dodecahedra (Figure 1, top left). These are fused by one Cl···Cl and two O···O edges to build up layers according to ${}^{2}_{\infty}\{[YCl^{e}_{2/2}O^{e}_{4/2}O^{t}_{2/1}]^{6}\text{-}\}$ (e = edge-sharing, t = terminal) parallel to the ab plane. The interatomic distances between the yttrium cations and the chloride as well as the oxide anions (Table 1) are within the range of those in other yttrium compounds consisting of Cl^- and O^{2-} anions, such as YCl_3[19] or ε-Y_2WO_6.[20] The likewise crystallographically unique W^{6+} cations represent the centers of *non*-con-

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Table 1. Motifs of mutual adjunction[22–24] and internuclear distances in the crystal structure of YCl[WO$_4$].

Atom	Cl	O1	O2	O3	CN
Y	2 / 2	1 / 1	1 / 1	4 / 2	8
d /pm	270.2(2)	230.4(7)	229.3(6)	228.2(4)	
	273.8(2)			260.8(4)	
W	0 / 0	1 / 1	1 / 1	2 / 1	4
d /pm		174.0(7)	175.8(5)	178.5(4)	
∢ /°		O2: 109.7(3)	O3: 111.6(2)	O3: 100.1(3)	
		O3: 111.8(2)			
CN	2	2	2	3	

densed [WO$_4$]$^{2-}$ tetrahedra (Figure 1, top right) exhibiting W^{6+}···O^{2-} distances and O^{2-}···W^{6+}···O^{2-} angles (Table 1), analogous to other compounds with tetrahedral tungstate units, e.g. K$_2$[WO$_4$].[21] The setup of the crystal structure can be described as the interconnection of the anionic $^2_\infty\{[\text{YCl}^e_{2/2}\text{O}^e_{4/2}\text{O}^t_{2/1}]^{6}\text{-}\}$ layers by W^{6+} cations along [001] (Figure 1, bottom).

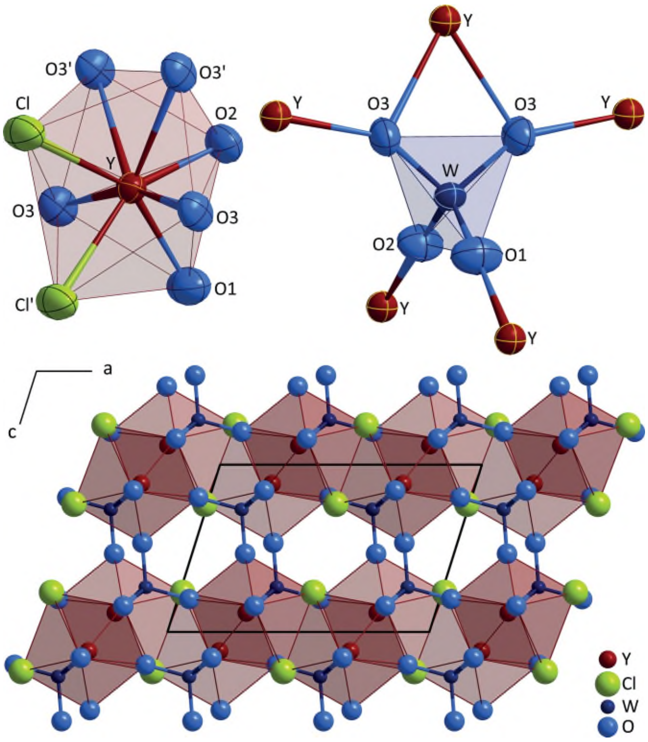

Figure 1. Anionic coordination around the Y^{3+} cations (top left), cationic coordination of the [WO$_4$]$^{2-}$ tetrahedra (top right), and view at the crystal structure of YCl[WO$_4$] along [010] (bottom). Ellipsoid representation at 95 % probability level.

Luminescence Properties

The doped title compound YCl[WO$_4$]:Tb^{3+} exhibits the expected bright green luminescence upon irradiation with UV light with the wavelength of λ = 254 nm (Figure 3, top). At this wavelength, excitation occurs in the O^{2-}→W^{6+} ligand-to-metal charge transfer (LMCT) region of the spectrum. The maximum of this transition shifts from 272 nm at room temperature to 267 nm at 77 K (see red curves in Figure 2, top and bottom). At the latter temperature, another signal becomes apparent, and a second one is visible as small shoulder. These can most likely be attributed to f→f transitions of Tb^{3+}, since they are not temperature dependent. According to *Dieke*[25] the ^{7}F$_6$→^{5}F$_5$ transition occurs at 288 nm and the ^{7}F$_6$→^{5}H$_6$

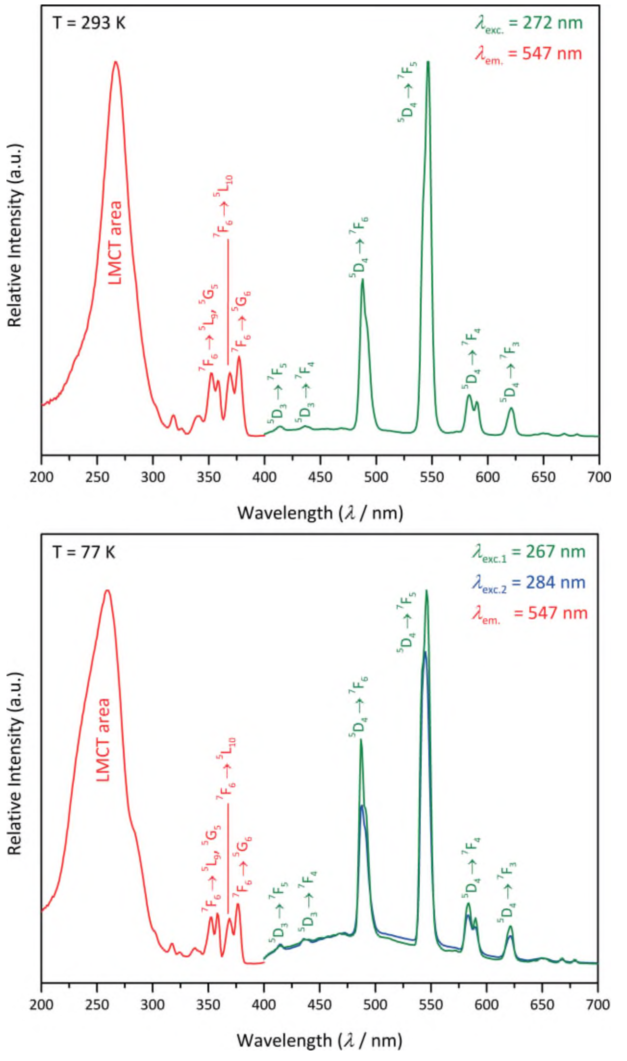

Figure 2. Excitation (red) and emission spectra (green, recorded at the O^{2-}→W^{6+} LMCT maximum in both cases and blue, recorded at the side maximum of the LMCT area at 284 nm, present in the spectrum at low temperature) of YCl[WO$_4$]:Tb^{3+} recorded at room temperature (top) and at 77 K (bottom).

transition is found at 302 nm. At room temperature, the $O^{2-}\rightarrow W^{6+}$ LMCT superimposes both transitions, although they can be adumbrated by the small shoulder around 300 nm (Figure 2, top and bottom). Furthermore, the typical f→f transitions from the $^7F_6$ ground state for Tb^{3+} are visible in all excitation spectra (red curves) in Figure 2 and Figure 3.[26]

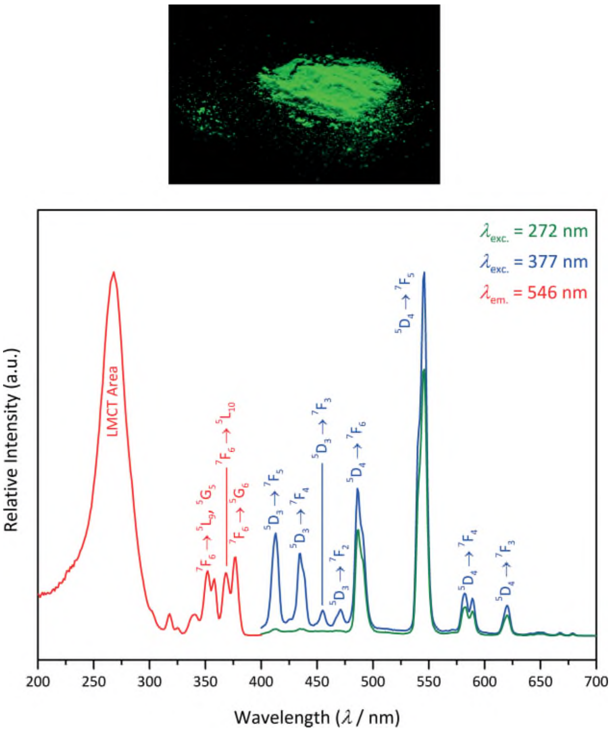

Figure 3. Bright green luminesence of $YCl[WO_4]:Tb^{3+}$ (top) upon irradiation with UV light (λ = 254 nm) as well as excitation (red) and emission spectra (bottom; green, recorded at the $O^{2-}\rightarrow W^{6+}$ LMCT maximum at 272 nm and blue, recorded at the largest f→f transition $^7F_6\rightarrow{}^5G_6$ present for the Tb^{3+} cations at 377 nm).

Regarding the $O^{2-}\rightarrow W^{6+}$ LMCT, which can clearly be used as sensitizer of the Tb^{3+} luminescence, an energy transfer mechanism to the activator must be discussed. Of the three fundamental possibilities of sensitizer-to-activator energy transfer, the *Dexter* mechanism[27] relies strongly on exchange interactions, hence a certain level of covalence between the sensitizer and the activator is needed. The contacts between Y^{3+} (and thus Tb^{3+}) and the surrounding anions are considered mainly of ionic nature (in contrast to the interactions between W^{6+} and O^{2-} with a strong covalent part), therefore this mechanism plays only a minor role (if any at all). In the *Förster* mechanism[28,29] the energy transfer is associated with a transition in the dipole moment and thus with the distance between the sensitizer and the activator group as one of the main contributors. The distance between the O^{2-} anions and the Y^{3+} and Tb^{3+} cations, respectively, is with four of the six mentioned contacts residing at about 229 pm (see Table 1) slightly lower than the sum of the ionic radii[30] of 237 pm for $r(Y^{3+}) + r(O^{2-})$. Since the Tb^{3+} cation displays an about 2 pm larger ionic radius than Y^{3+} their contact is even closer and the influence of an energy transfer according to the *Förster* theory is very likely.

The third possibility, luminescence emission of the sensitizer (here the $[WO_4]^{2-}$ units) as excitation source for the f→f transitions in the activator (here Tb^{3+}) is basically possible, due to oxidotungstates being known for their bluish-white LMCT emission. In case of tetrahedral units, its maximum lies between 450 and 500 nm[31] (see Figure 2, bottom), which does mainly coincide with the $^7F_5\rightarrow{}^5D_4$ transition in Tb^{3+}. Thus, a direct excitation into this level by the $O^{2-}\rightarrow W^{6+}$ LMCT emission is a good explanation for the $^5D_4\rightarrow{}^7F_J$ emissions being far more prominent than from the $^5D_3$ level by exciting via the $O^{2-}\rightarrow W^{6+}$ LMCT. The overall excitation by the latter process is also less dominant in $YCl[WO_4]:Tb^{3+}$ than in tungstates with larger or condensed units, which show a smaller Stokes shift between the maximum of the LMCT excitation and emission as seen in e.g. $Gd_3Cl_3[WO_6]$ with trigonal prismatic $[WO_6]^{6-}$ entities.[17] In Figure 3 (bottom) two emission spectra are displayed, one excitated at 272 nm, utilizing the $O^{2-}\rightarrow W^{6+}$ LMCT and the other excited at 377 nm, the most intense f→f transition in the excitation spectrum of the title compound. The excitation at the shorter wavelength results in the emissions from the $^5D_4$ excited state being recordable almost exclusively with the $^5D_4\rightarrow{}^7F_5$ at λ = 546 nm being the strongest one, easily explaining the green luminescence upon irradiation in the UV range (green curve in Figure 3, bottom). The basic intensity ratio of the $^5D_4\rightarrow{}^7F_J$ transitions do not change if the emission is excited at 377 nm, however the $^5D_3$ excited state is also populated to a certain extend. Hence, the $^5D_3\rightarrow{}^7F_{2-5}$ emission lines show significant intensity, creating a blue shift in the visible luminescence (blue curve in Figure 3, bottom) and thus show only little or no occurrence of cross relaxation. The excitation at 284 nm as seen in Figure 2 (bottom) also displays a very small albeit detectable rise in the emissions from the $^5D_3$ state. This supports the assumption that the side maximum at this wavelength is a superposition of the $O^{2-}\rightarrow W^{6+}$ LMCT and a f→f transition. Although no quantum yield measurements were performed, it is clearly visible that the $O^{2-}\rightarrow W^{6+}$ LMCT shows significantly higher intensity than the parity forbidden f→f transitions in the excitation spectra. Thus, the presented material might not be the brightest luminophore, however, it definitely shows potential.

Experimental Section

Synthesis: The admixture of yttrium sesquioxide (Y_2O_3: 99.9 %, ChemPur, Karlsruhe, Germany), yttrium trichloride (YCl_3: 99.9 %, ChemPur, Karlsruhe, Germany), and tungsten trioxide (WO_3: p. a., Merck, Darmstadt, Germany) in molar ratio 1:5:3 was annealed for 6 d at a temperature of 850 °C in evacuated silica ampules. The reaction takes place according to the following equation:

$$Y_2O_3 + YCl_3 + 3\ WO_3 \rightarrow 3\ YCl[WO_4]$$

with an excess of YCl_3, which was used as flux, removed from the crude product by washing with water. Besides several colorless and transparent single crystals, $YCl[WO_4]$ emerged as single phase microcrystalline powder. To synthesize the Tb^{3+}-doped material, about 1 % of Y_2O_3 was substituted by Tb_2O_3, which was synthesized from Tb_4O_7 (99.9 %, ChemPur, Karlsruhe, Germany) in a continuous stream of argon containing 7.5 % of H_2.

Single Crystal X-ray Diffraction: Suitable single crystals of the title compound were investigated with a Nonius κ-CCD diffractometer (Bruker, Karlsruhe, Germany), operating with graphite-monochromatized Mo-K_α radiation (λ = 71.07 pm). Structure solution and refinement was conducted with the help of the program package SHELX-2013,[32] applying structure factors according to International Tables for Crystallography, vol. C.[33] Besides corrections of background, polarization and Lorentz factors, a numerical absorption correction was performed by the program HABITUS.[34] Further details on the crystal structure refinement are summarized in Table 2

Table 2. Crystallographic data for YCl[WO_4].

	YCl[WO_4]
Crystal system	monoclinic
Space group	*C*2/*m* (no. 12)
Formula units	4
Lattice parameters	
a /pm	1022.41(3)
b /pm	722.91(2)
c /pm	684.34(2)
β /°	107.455(3)
Molar volume, V_m /cm^3·mol^{-1}	72.64
Calculated density, D_x /g·cm^{-3}	5.124
Absorption coefficient, μ /mm^{-1}	36.23
F(000)	648
Diffraction angle, Θ_{max} / deg	28.22
Index range, $\pm h_{max}$ / $\pm k_{max}$ / $\pm l_{max}$	13 / 9 / 9
Collected / unique reflections	5371 / 635
Parameters	41
R_{int} / R_σ	0.114 / 0.046
R_1 for (#) reflections with $\lvert F_o \rvert \geq 4\sigma(F_o)$	0.024 (607)
R_1 / wR_2 for all reflections	0.026 / 0.055
Goodness-of-fit, *S*	1.013
Extinction coefficient, *g*	0.0123(6)
Min. / max. residual electron density, ρ /e^-·10^{-6} pm^{-3}	–1.28 / 2.14

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@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository number CSD-434688.

X-ray Powder Diffraction: X-ray powder patterns of microcrystalline samples of both YCl[WO_4] and YCl[WO_4]:Tb^{3+} (Figure 4) were collected with a STADI P powder diffractometer (Stoe & Cie, Darmstadt, Germany) equipped with a position sensitive detector using germanium-monochromatized Cu-K_α radiation (λ = 154.06 pm). Rietveld refinement[35] of the powder patterns was conducted with the help of the program WINPLOTR.[36] The slight deviations between the measured and theoretical intensities visible in the difference line of Figure 4 (blue) can be attributed to texture effects.

Photoluminescence Spectroscopy: Solid-state excitation and emission spectra of YCl[WO_4]:Tb^{3+} were recorded at room temperature with a Horiba FluoroMax-4 fluorescence spectrometer equipped with a xenon discharge lamp scanning a range from 200 to 800 nm. The excitation spectra were corrected with respect to the lamp intensity. Low temperature measurements were performed with a liquid nitrogen dewar assembly within the same device. Electronic transitions were assigned according to the energy-level diagram of the trivalent terbium cations.[25,26]

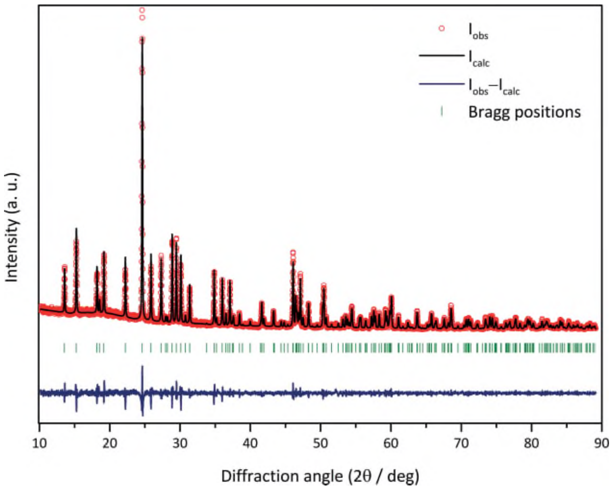

Figure 4. Rietveld refined powder pattern of YCl[WO_4]:Tb^{3+}.

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Keywords: Yttrium; Chloride; Tungstate; Crystal structure; Luminescence

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