



Upconversion luminescence of Tm^{3+} sensitized by Yb^{3+} ions in monoclinic $\text{KGd}(\text{WO}_4)_2$ single crystals

F. Güell^a, R. Solé^a, Jna. Gavalda^a, M. Aguiló^a, M. Galán^b, F. Díaz^a, J. Massons^{a,*}

^a Física i Cristal·lografia de Materials (FiCMA), Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Campus Sescelades, Cl. Marcel·lí Domingo, s/n 43007 Tarragona, Catalunya, Spain

^b Monocrom S.L., Vilanoveta 6, 08800 Vilanova i la Geltrú, Catalunya, Spain

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Abstract

We observed a significant blue emission at 476 nm in Tm^{3+} and Yb^{3+} -codoped $\text{KGd}(\text{WO}_4)_2$ monoclinic single crystals by pumping at 940 nm. The single crystals were grown using the top-seeded-solution-growth slow-cooling method (TSSG). We also report thulium emissions at 650 nm, 802 nm and 1.48 μm . The emission spectra are characterized as a function of the Tm^{3+} and Yb^{3+} ions concentration and temperature from 6 K to room temperature. The energy upconversion excitation mechanism for thulium emitting levels is assigned to a cooperative energy transfer process by the ytterbium-sensitizer ions.

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1. Introduction

Intensive research has recently been dedicated to obtain laser radiation in the visible spectrum. Frequency upconversion in rare-earth doped solid-state materials can provide an efficient mechanism to obtain blue and green laser radiation [1]. Blue upconversion emissions can be generated by Tm^{3+} -doped materials from the electronic transitions $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ around 450 and 480 nm, respectively.

$\text{KGd}(\text{WO}_4)_2$ single crystals (hereafter KGdW) are good hosts for rare-earth ions for the development of solid-state lasers [2–5]. These crystals have a monoclinic crystallographic structure, which provides a strong physical anisotropy and makes it possible to obtain polarized laser radiation. They also allow the easy introduction of optically active ions, Gd^{3+} ions can be efficiently substituted by Tm^{3+} and Yb^{3+} ions.

The energy transfer mechanisms between Yb^{3+} and Tm^{3+} ions are well known. Codoping with Yb^{3+} and Tm^{3+} ions significantly increases upconversion yield owing to an efficient energy transfer from ytterbium to thulium [6]. The advantages of Yb^{3+} ions are that they absorb in the near-infrared region around 940–980 nm, where laser diodes work efficiently. Moreover, Yb^{3+} ions are good sensitizers of Tm^{3+} ions [7], for which laser operation has already been achieved in the blue region by upconversion around 480 nm [8], and in the infrared region around 1.5 μm [9], 1.9 μm [10] and 2.3 μm [11].

Upconversion mechanisms are multi-photon processes in which two or more near-infrared photons are needed to generate a shorter wavelength photon. The phenomenon of upconversion in rare-earth ions (Tm^{3+} and Yb^{3+}) was first observed by Ovsyankin and Feofilov [12], and it was called cooperative sensitization of fluorescence. Auzel and Acad [13] interpreted the process as a successive energy transfer from Yb^{3+} to Tm^{3+} by which the first near-infrared photon converts the system into an intermediate metastable state from which the system is excited to a higher energy level due to absorption of the second photon. Blue emission

* Corresponding author. Tel.: +34 977559519; fax: +34 977559563.
E-mail address: jaume.massons@urv.net (J. Massons).

around 480 nm from Tm^{3+} ions sensitized by Yb^{3+} ions upon 980 nm excitation has been observed in different hosts [14–18]. The process involves a three-step absorption of photons due to energy transfer from the $^2\text{F}_{5/2}$ level of Yb^{3+} to the $^3\text{H}_5$, $^3\text{F}_2 + ^3\text{F}_3$ and $^1\text{G}_4$ levels of Tm^{3+} .

In this paper, we study the luminescence of Tm^{3+} sensitized by Yb^{3+} ions in monoclinic KGdW single crystals by exciting at 940 nm. We analyze the luminescence of Tm^{3+} ions as a function of the Tm^{3+} and Yb^{3+} concentrations and the temperature from 6 K to room temperature. Finally, we propose an upconversion scheme for the luminescence generation of the Tm^{3+} ions.

2. Experimental

We grew good-optical-quality and inclusion-free single crystals of KGdW codoped with Tm^{3+} and Yb^{3+} ions at

Table 1
Composition of the $\text{KGd}(\text{WO}_4)_2$ single crystals

$[\text{Tm}^{3+}] (\times 10^{20} \text{ at/cm}^3 \text{ in the crystal})$	$[\text{Yb}^{3+}] (\times 10^{20} \text{ at/cm}^3 \text{ in the crystal})$	Stoichiometric formula
0.44 ± 0.09	0.6 ± 0.2	$\text{KGd}_{0.984}\text{Tm}_{0.007}\text{Yb}_{0.009}(\text{WO}_4)_2$
0.38 ± 0.07	0.8 ± 0.1	$\text{KGd}_{0.982}\text{Tm}_{0.006}\text{Yb}_{0.012}(\text{WO}_4)_2$
0.38 ± 0.07	1.4 ± 0.1	$\text{KGd}_{0.972}\text{Tm}_{0.006}\text{Yb}_{0.022}(\text{WO}_4)_2$
0.38 ± 0.07	2.3 ± 0.1	$\text{KGd}_{0.957}\text{Tm}_{0.006}\text{Yb}_{0.037}(\text{WO}_4)_2$
0.88 ± 0.08	1.3 ± 0.1	$\text{KGd}_{0.965}\text{Tm}_{0.014}\text{Yb}_{0.021}(\text{WO}_4)_2$
0.88 ± 0.08	2.2 ± 0.1	$\text{KGd}_{0.951}\text{Tm}_{0.014}\text{Yb}_{0.035}(\text{WO}_4)_2$
1.26 ± 0.07	2.3 ± 0.1	$\text{KGd}_{0.943}\text{Tm}_{0.020}\text{Yb}_{0.037}(\text{WO}_4)_2$
1.32 ± 0.08	3.4 ± 0.1	$\text{KGd}_{0.925}\text{Tm}_{0.021}\text{Yb}_{0.054}(\text{WO}_4)_2$
1.58 ± 0.09	5.6 ± 0.1	$\text{KGd}_{0.887}\text{Tm}_{0.025}\text{Yb}_{0.088}(\text{WO}_4)_2$

several dopant concentrations by the top-seeded-solution-growth slow-cooling method (TSSG) using $\text{K}_2\text{W}_2\text{O}_7$ as solvent according to the method described elsewhere [19,20]. Powdered precursors of KGdW: Tm^{3+} – Yb^{3+} single crystals were K_2CO_3 , Gd_2O_3 , Tm_2O_3 , Yb_2O_3 and WO_3 (Fluka, 99.9% pure). These were used to synthesize these types of single crystals at several Tm^{3+} and Yb^{3+} ions concentrations, $\text{KGd}_{1-x-y}\text{Tm}_x\text{Yb}_y(\text{WO}_4)_2$, with a binary solution composition of 11.5 mol.% solute/88.5 mol.% solvent. Table 1 summarizes the dopant concentrations of Tm^{3+} and Yb^{3+} ions in the crystals measured by electron probe micro analysis (EPMA). The optical samples were cut

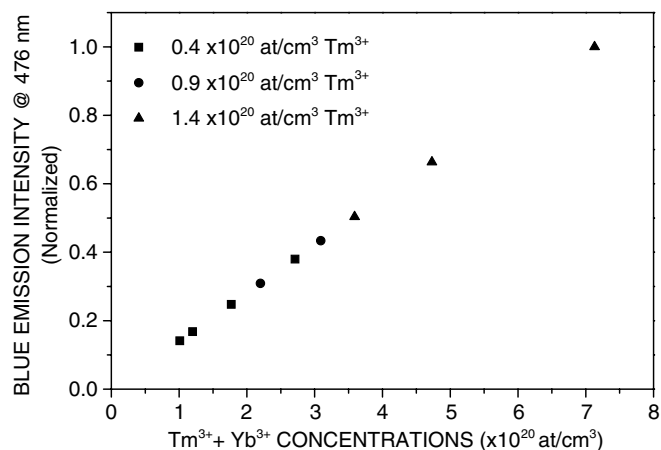


Fig. 1. Blue emission intensity as a function of the combined Tm^{3+} and Yb^{3+} dopant concentration in KGdW single crystals.

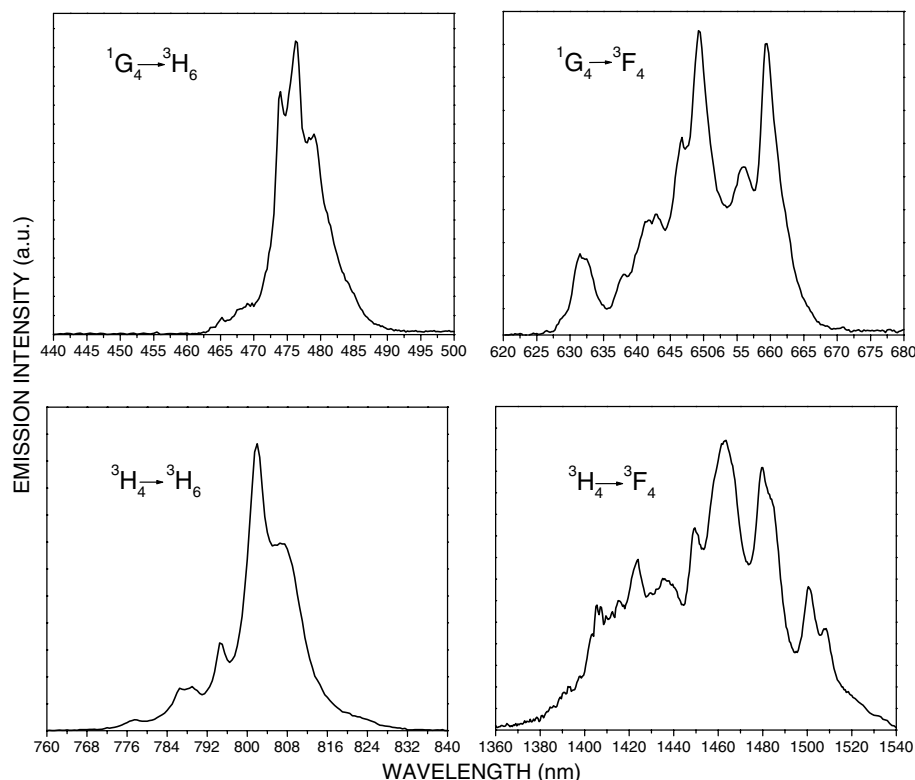


Fig. 2. Room temperature emission spectra for a $\text{KGd}_{0.887}\text{Tm}_{0.025}\text{Yb}_{0.088}(\text{WO}_4)_2$ single crystal by exciting at 940 nm.

and oriented for polarized laser excitation parallel to N_m and propagation along N_p axis.

The experimental measurements for the emission spectra were obtained with an Optical Parametric Oscillator, VEGA 100, pumped by the third harmonic of a Q-switched YAG:Nd laser (pulse duration: 7 ns, repetition rate: 10 Hz), SAGA 120, from B.M. Industries. The optical excitation was also carried out by a diode laser (pump emission 940 nm, power 750 mW, electronically chopped at 30 Hz), from Monocrom S.L.. Fluorescence was dispersed through a HR460 Jobin Yvon-Spex monochromator (focal length 460 mm, f/5.3, spectral resolution 0.05 nm). The detectors applied are Hamamatsu: R928 and R5509-72 photomultipliers, and were connected to a Perkin Elmer 7265 DSP lock-in amplifier. Cryogenic temperatures were achieved with a Leybold RDK 6-320 closed cycle helium cryostat.

3. Results and discussion

First, we studied the blue emission intensity as a function of the Tm^{3+} and Yb^{3+} concentrations (see Fig. 1). We found that, at a fixed Tm^{3+} concentration, the intensity of the blue luminescence increased as the Yb^{3+} concentration increased. Also, the intensity of the blue luminescence increased as the Tm^{3+} and Yb^{3+} concentrations increased. The same behavior was also observed for the 650 nm, 802 nm and 1.48 μm emissions intensity. Quenching phenomena of luminescence due to higher Tm^{3+} and Yb^{3+} concentrations were not observed in the samples we studied.

Fig. 2 shows the RT emission spectra for a $KGd_{0.887}Tm_{0.025}Yb_{0.088}(WO_4)_2$ single crystal. The significant blue emission at 476 nm and the 650 nm emission, corresponding to the transitions from the 1G_4 to the 3H_6 and 3F_4 levels, respectively, show that the 1G_4 level was strongly populated at RT. The decay from the 3H_4 to the 3H_6 and 3F_4 levels generated the 802 nm and 1.48 μm emissions, respectively. In addition to the emissions reported, we also detected a weak emission in the blue range at 454 nm, corresponding to the $^1D_2 \rightarrow ^3F_4$ transition, because the 1D_2 level was slightly populated by exciting at 940 nm, as we have observed previously in Tm^{3+} -doped $KYb(WO_4)_2$ single crystals [14].

We analyzed how the emission channels evolved with temperature in KGdW single crystals. Fig. 3 shows the low temperature (6 K) emission spectra of the $^1G_4 \rightarrow ^3H_6$,

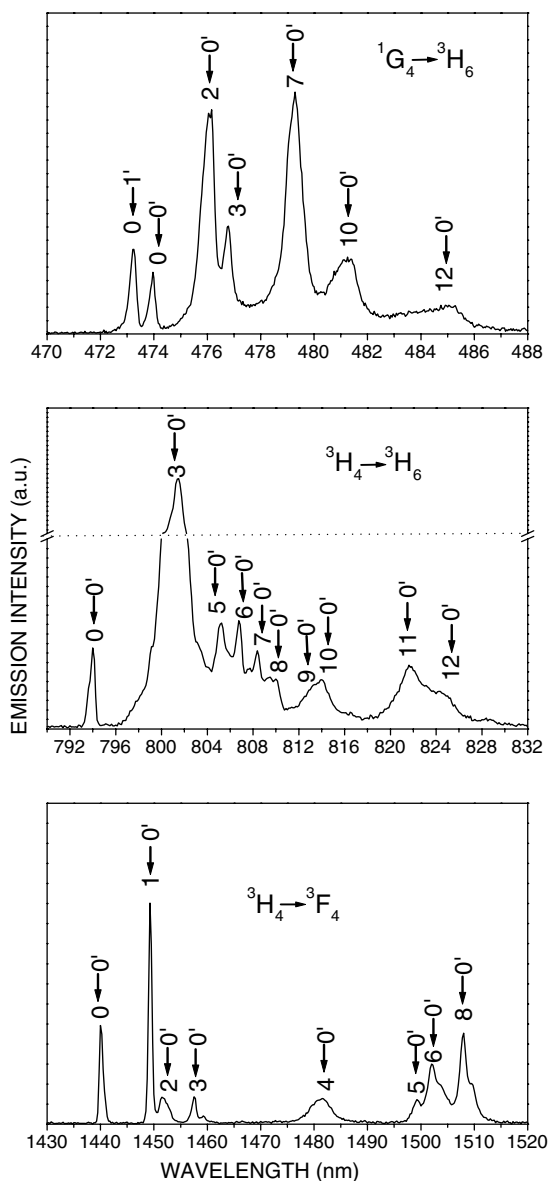


Fig. 3. Low temperature (6 K) emission spectra for a $KGd_{0.887}Tm_{0.025}Yb_{0.088}(WO_4)_2$ single crystal by exciting at 940 nm.

Table 2

Electronic transitions of the Stark sublevels obtained at 6 K

λ (nm)	E (cm^{-1})	Electronic transition
473.3	21128	$^1G_4(1') \rightarrow ^3H_6(0)$
474.0	21097	$^1G_4(0') \rightarrow ^3H_6(0)$
476.2	20999	$^1G_4(0') \rightarrow ^3H_6(2)$
476.8	20973	$^1G_4(0') \rightarrow ^3H_6(3)$
479.3	20864	$^1G_4(0') \rightarrow ^3H_6(7)$
481.3	20777	$^1G_4(0') \rightarrow ^3H_6(10)$
484.8	20627	$^1G_4(0') \rightarrow ^3H_6(12)$
794.1	12592	$^3H_4(0') \rightarrow ^3H_6(0)$
801.5	12477	$^3H_4(0') \rightarrow ^3H_6(3)$
805.3	12418	$^3H_4(0') \rightarrow ^3H_6(5)$
806.7	12396	$^3H_4(0') \rightarrow ^3H_6(6)$
808.5	12369	$^3H_4(0') \rightarrow ^3H_6(7)$
810.0	12346	$^3H_4(0') \rightarrow ^3H_6(8)$
813.5	12292	$^3H_4(0') \rightarrow ^3H_6(9)$
814.6	12276	$^3H_4(0') \rightarrow ^3H_6(10)$
821.6	12171	$^3H_4(0') \rightarrow ^3H_6(11)$
824.3	12131	$^3H_4(0') \rightarrow ^3H_6(12)$
1440	6944	$^3H_4(0') \rightarrow ^3F_4(0)$
1449	6901	$^3H_4(0') \rightarrow ^3F_4(1)$
1452	6887	$^3H_4(0') \rightarrow ^3F_4(2)$
1458	6859	$^3H_4(0') \rightarrow ^3F_4(3)$
1481	6752	$^3H_4(0') \rightarrow ^3F_4(4)$
1499	6671	$^3H_4(0') \rightarrow ^3F_4(5)$
1502	6658	$^3H_4(0') \rightarrow ^3F_4(6)$
1508	6631	$^3H_4(0') \rightarrow ^3F_4(8)$

${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ and ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transitions for a $\text{KGd}_{0.887}\text{Tm}_{0.025}\text{Yb}_{0.088}(\text{WO}_4)_2$ single crystal. To better present our results of the ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ transition, we made a break in the vertical scale because of the high intensity of the peak at 801.7 nm. Table 2 summarizes the peaks observed, which correspond to the electronic transitions from the energy sublevels. In this table, the n Stark sublevels, increasing from 0 to n in energy (n' for the upper sublevel and n for the lower sublevel) are labeled. These results show a small shift with the corresponding energies of the Stark sublevels of the ${}^3\text{F}_4$ and ${}^3\text{H}_6$ states obtained in our previous studies [21,22] due to the incorporation of Yb^{3+} ions in the KGdW single crystals. The intensity of these emissions decreased slightly as the temperature increased.

To better understand the mechanism that produced the upconversion luminescence, we investigated the dependence of the blue emission at 476 nm on the incident laser excitation power at 940 nm using the laser diode under a pump power ranging from 160 mW to 720 mW. The beam was focused to a diameter of 50 μm . Fig. 4 shows a quasi-quadratic dependence of the blue intensity on the pump power for a $\text{KGd}_{0.887}\text{Tm}_{0.025}\text{Yb}_{0.088}(\text{WO}_4)_2$ single crystal. The double-logarithmic representation shows a slope (N) of about 1.7, which suggests that the mechanism for generating the blue emission at 476 nm involves at least two photons. This approach is consistent with the scheme proposed by Ovsyankin and Feofilov for thulium sensitized by ytterbium [12]. At low pump power, the slope of the emission intensity versus incident pump power is equal to the order of the excitation process (1.9) and at high pump power it drops to 1.5. These values are consistent with the theoretical limits and are less than 2 due to the excitation density [23] as could be predicted for simple two-photon absorption processes.

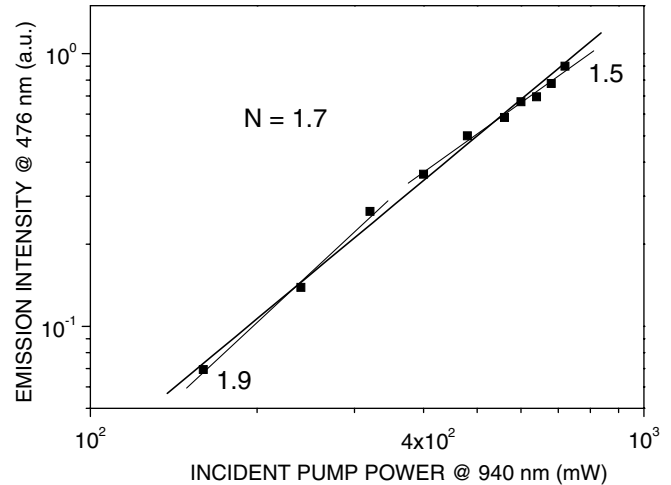


Fig. 4. Double-logarithmic representation of the blue 476 nm upconversion emission intensity as a function of the excitation power at 940 nm.

Fig. 5 shows a partial energy-level diagram of Tm^{3+} and Yb^{3+} ions in KGdW single crystals [22,24]. The pumping at 940 nm excited only the Yb^{3+} ions, the electronic population was excited from the ground state ${}^2\text{F}_{7/2}$ to the ${}^2\text{F}_{5/2}$ energy level. By pumping at 940 nm there is a simultaneous interaction of two Yb^{3+} ions in the excited state ${}^2\text{F}_{5/2}$, which transferred its energy to the ${}^1\text{G}_4$ energy level of Tm^{3+} ions (${}^2\text{F}_{5/2} + {}^2\text{F}_{5/2} + {}^3\text{H}_6 \rightarrow {}^2\text{F}_{7/2} + {}^2\text{F}_{7/2} + {}^1\text{G}_4$) (see Fig. 5). The decay from the ${}^1\text{G}_4$ to the ${}^3\text{H}_6$ and ${}^3\text{F}_4$ levels generated the emissions at 476 and 650 nm, respectively. The emissions at 802 nm and 1.48 μm were generated due to the decay from the ${}^3\text{H}_4$ to the ${}^3\text{H}_6$ and ${}^3\text{F}_4$ levels, respectively.

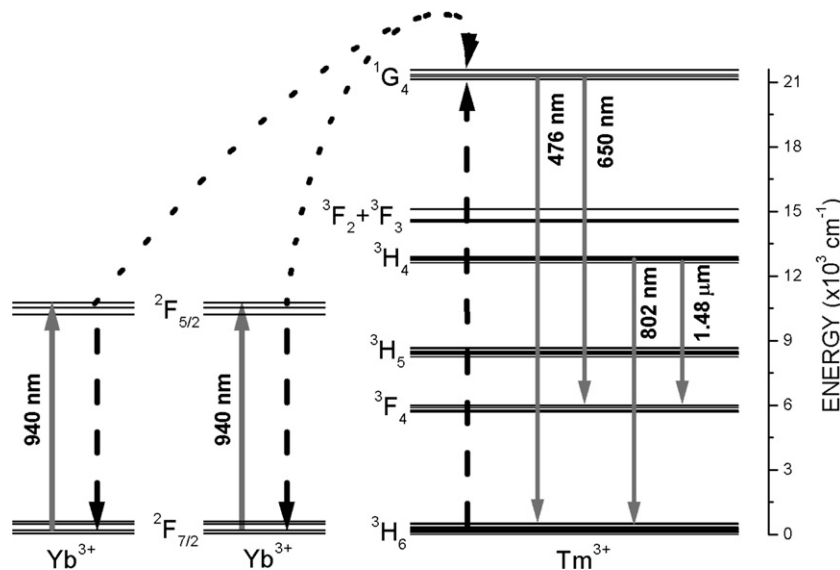


Fig. 5. Partial energy-level diagram depicting the upconversion mechanisms of Tm^{3+} sensitized by Yb^{3+} ions and generation of the Tm^{3+} emissions by exciting at 940 nm.

4. Conclusions

We grew Tm^{3+} and Yb^{3+} -codoped KGdW single crystals at several Tm^{3+} and Yb^{3+} ions concentrations. We characterize the luminescence of Tm^{3+} ions by exciting the Yb^{3+} ions at 940 nm. We observed a significant blue emission at 476 nm in Tm^{3+} and Yb^{3+} -codoped KGdW single crystals that increased as the Yb^{3+} concentration increased. Taking into account the observed slope (1.7), we propose that the most likely energy transfer process between ytterbium and thulium ions involves at least two photons, and that the upconversion scheme for generating the emissions of Tm^{3+} ions in KGdW codoped with Tm^{3+} and Yb^{3+} ions based on the successive absorption of two photons by cooperative sensitization.

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