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Yb^{3+} and Yb^{3+}-Eu^{3+} luminescent properties of the $Li_2Lu_5O_4(BO_3)_3$ phase.

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Abstract

The luminescence of Yb^{3+} in the oxyborate $Li_2Lu_5O_4(BO_3)_3$ is reported. At low temperature, in addition to the usual ytterbium infrared emission, this phosphor presents an emission in the ultraviolet (λ_{max}= 345 nm) which corresponds to the transition from the charge transfer state (O-Yb) to the 4f levels of Yb^{3+}. The temperature quenching Tq50% is equal to 120K. The infrared emission studied at room temperature is located between 950 and 1100 nm.

An europium emission quenching in the $Li_2Yb_5O_4(BO_3)_3$ phase is related to an Eu→Yb transfer by cross-relaxation. The reverse Yb→Eu transfer by cooperative sensitization is highlighted in the codoped $Li_2Lu_5O_4(BO_3)_3$ compound.

PACS:

Keys words: oxyborate, luminescence, ytterbium, europium, cooperative sensitization

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Introduction

The interest in borates by the scientific community is certain. Due to increasing demands in new efficient phosphors for applications in plasma display panels, the rare earth borates' properties have attracted attention [1]. Cerium-activated borates are candidates as scintillators for the detection of neutrons [2]. In ultraviolet applications, borates are superior to other commonly used non linear optical materials ($LiNbO_3$) because of their high ultraviolet transmittance at short wavelengths combined with a high damage threshold [3]. We cannot conclude this non exhaustive list without mentioning the laser properties of the rare earth activated oxyborates Yb:GdCOB [4].

In the pseudo-ternary diagrams R_2O_3-B_2O_3-Li_2O (R= lanthanides, Y) we have found new oxyborates of formula $Li_2Ln_5O_4(BO_3)_3$ for Ln= Yb, Lu [5]. In this study are reported luminescent properties of the Yb^{3+} and Yb^{3+}-Eu^{3+} activated lutetium phase. In particular it was of interest to determine whether Yb^{3+} showed a charge transfer luminescence in an oxyborate. Such a luminescence presents an new interest as scintillators for the detection of solar neutrinos [6;7]. It has been observed in various oxide lattices but not in the borate RBO_3.

Powder preparation

All the reactants were mixed in stoichiometric proportions and dissolved in nitric acid. After drying, the products were heated at 400 °C until all nitric vapors disappeared, then at 700°C during 4h and 900°C during 12h. The final products were controlled by X-ray diffraction.

Experimental measurements

Ultraviolet luminescent properties were studied using a SPEX Fluorolog FL 212 spectrofluorimeter. Excitation spectra were corrected from the variation of the incident flux as well as emission spectra from the transmission of the monochromator and from the response of the photomultiplier.

The infrared luminescence was recorded on an Edinburgh Instruments spectrofluorimeter FL900CDT with a M30 monochromator connected to a AD 403L germanium detector. The UV decay curves were performed on the same equipment using a nano-pulse hydrogen lamp as a source.

The IR lifetime was performed with an OPO system (GWU355SH) pumped with a YAG:Nd 10Hz continuum Surelite.

Experimental results

1. Luminescent properties of $Li_2Lu_5O_4(BO_3)_3$: Yb^{3+}

Ultraviolet luminescence

The introduction of ytterbium in the oxyborate $Li_2Lu_5O_4(BO_3)_3$ induces an absorption band in the UV range due to the oxygen-ytterbium charge transfer transition. In the compound $Li_2Lu_5O_4(BO_3)_3$, the rare earth is located in five independant crystallographic positions which correspond to seven-coordinated environments. This absorption band is associated to the substitution of the lutetium by the ytterbium in the different types of polyhedra but as they are very similar in a point of view of the rare earth-oxygen distances, we can consider that only one broad absorption band can be distinguished. For an excitation in this band, the emission process to the ground state, also called charge transfer emission, occurs at low temperature.

The excitation and emission spectra at 6 K are shown in figures 1. The charge transfer band is present in the excitation spectrum at 230 nm and around 220 nm, another band is

present and can be ascribed to an excitation through the host matrix (valence to conduction band transition). The emission spectrum contains two bands corresponding to the deexcitation from the charge transfer states (CTS) to the 4f levels of ytterbium, $^2F_{7/2}$ and $^2F_{5/2}$ at 345 and 520 nm respectively. They are separated by about 9750 cm^{-1} which is in good agreement with the energy difference of the two 4f levels. At room temperature the ultraviolet luminescence is not totally quenched but the emission is strongly affected by the temperature: 50 % of the maximum of the intensity emission observed at 6 K is quenched at 120 K ($T_{50\%}$= 120 K). The variation of the integrated emission as a function of the temperature is also reported in the figure 1. If we consider these levels (CTS and Yb^{3+} 4f levels) in a coordinate configurational diagram representation, the emission stability depends on the energy difference between the lowest excited state of the CTS and its intersection with the parabola associated with the $^2F_{5/2}$ level. In the oxyborate, electronic transfer come either from oxygen atoms of borate groups or from oxygen atoms coordinated tetrahedrally to rare earth ions. The lower-energy CT transitions are likely those from oxygen ions not bound to boron atoms [5, 8]. The Yb^{3+} CTB emission stability in $Li_2Lu_5O_4(BO_3)_3$ is similar to that observed in Y_2O_3 ($T_{50\%}$= 130 K) whose absorption maximum is situated at 227 nm [9,10]. The emission and excitation spectra of the oxide Lu_2O_3: Yb^{3+} 1% ($Lu_{1.98}Yb_{0.02}O_3$) are presented in figure 2. Yb^{3+} luminescence behaviour of the oxyborate is close to that observed for both oxides. The Stokes shift (SS), which is defined as the energy difference between the position of the maxima of the bands in the excitation and emission spectra is equal to about 14500 cm^{-1} for the oxyborate $Li_2Lu_5O_4(BO_3)_3$: Yb^{3+} and to 14400 cm^{-1} for the oxide Lu_2O_3: Yb^{3+}. These values are comparable to those observed in other oxide lattices [10].

The lifetime of the ultraviolet emission (λ_{exc}= 230 nm, λ_{em}= 345 nm) is equal to 80 ns at 10 K. This value is also in the order of magnetitude of those observed by L. van Pieterson et al [10]. These lifetimes of the Yb^{3+} CT emission are longer than those expected for an

allowed transition: the small overlap between the wave functions of the electron on the cation and the hole on the ligand may be the cause of a decrease of the transition probability [9].

Infrared luminescence

At lower energy, in addition to the UV emission of Yb^{3+}, an infrared one corresponding to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transitions has been observed between 950 and 1100 nm at room temperature for an excitation in the CTB (Fig.3). The IR emission is composed of lines corresponding to transitions from the lower Stark levels of $^2F_{5/2}$ to the various component of $^2F_{7/2}$, the most intense one peaking at 973 nm.

Decay time measurements were performed at room temperature for an excitation at 980 nm and an emission at 1030 nm. The decay curve which corresponds to 4f-4f forbidden transitions ($\Delta l=0$) can be fitted with a single exponential leading to a lifetime equal to 1.02 ms.

2. Luminescent properties of the Yb^{3+}, Eu^{3+} co-doped $Li_2Lu_5O_4(BO_3)_3$ compound

2.1 $Eu^{3+} \rightarrow Yb^{3+}$ energy transfer

Luminescence studies carried out on $Li_2Lu_5O_4(BO_3)_3$: Eu^{3+} [11] and $Li_2Yb_5O_4(BO_3)_3$: Eu^{3+} have shown that europium emission in the ytterbium phase is considerably reduced compared to that observed in the lutetium one. This is observed for both excitation at 270 nm in the $O^{2-}\rightarrow Eu^{3+}$ CTB or at 394 nm in a 4f→4f absorption line of Eu^{3+} for Eu concentration of 10 mol%. The $Li_2Lu_5O_4(BO_3)_3$: Eu^{3+} presents a maximum of the Eu^{3+} intensity peaking at 609 nm.

The europium and ytterbium co-doped lutetium phase was studied to understand this phenomenon. Small amounts of activators were used in order to avoid concentration

quenching: 1% Yb^{3+} and 0.25 or 1% Eu^{3+} were substituted for lutetium in the oxyborate $Li_2Lu_5O_4(BO_3)_3$.

The mechanism, which is proposed to interpret the europium quenching and $Eu^{3+}\rightarrow Yb^{3+}$ energy transfer, is a cross-relaxation between the $^5D_0$-$^7F_6$ europium levels (~12000 cm^{-1}) and the $^2F_{7/2}$-$^2F_{5/2}$ ytterbium levels (~10000 cm^{-1}) (Figure 4). The difference between the two energy gaps may be compensated by phonon emission. We have presented in figure 5 the excitation spectra of the following emissions: the ultraviolet luminescence (λ_{em}=345 nm) of the compound $Li_2Lu_5O_4(BO_3)_3$:Yb^{3+} 1% (a. $Li_2Lu_{4.95}Yb_{0.05}O_4(BO_3)_3$), the infrared emission (λ_{em}=973 nm) of the Yb-Eu co-doped compositions $Li_2Lu_5O_4(BO_3)_3$:Yb^{3+} 1% and Eu^{3+} 0.25% (b. $Li_2Lu_{4.9375}Yb_{0.05}Eu_{0.0125}O_4(BO_3)_3$) or 1% (c. $Li_2Lu_{4.9}Yb_{0.05}Eu_{0.05}O_4(BO_3)_3$) and the europium luminescence in the visible range (λ_{em}=609 nm [11]) in the Yb-Eu co-doped compound $Li_2Lu_5O_4(BO_3)_3$:Yb^{3+} 1%, Eu^{3+} 1% (d. $Li_2Lu_{4.9}Yb_{0.05}Eu_{0.05}O_4(BO_3)_3$). For the b) and c) spectra, the excitation spectra associated with the infrared emission of ytterbium clearly show the O→Eu CTB at 260 nm. The 4f→4f absorption lines of europium can also be distinghished in the UV range. At a constant Yb^{3+} concentration, the infrared emission of ytterbium increases with the concentration of europium in the lutetium lattice (Fig.6). Excitation was performed at 285 nm in order to be sure that the observed emission is only due to the transfer from the europium ions. Similar results can be observed for excitation at 394 nm in an europium 4f-4f absorption line.

The $Eu^{3+} \rightarrow Yb^{3+}$ energy transfer in the oxide Y_2O_3 was reported by N.S. Yamada et al. in 1972 [12]. At N_2 liquid temperature, the difference energy between the $^5D_0$-$^7F_6$ levels of europium and the $^2F_{7/2}$-$^2F_{5/2}$ levels of ytterbium is equal to 1690 cm^{-1} which corresponds to the emission of four phonons (phonon energy in this lattice: 400 cm^{-1}). The transfer rate is equal to 17 s^{-1} for donor and acceptor concentrations respectively equal to 1 and 4%. The transfer rate between holmium and thulium in the same lattice amounts to 18000 s^{-1}, the energy

difference (460cm^{-1}) corresponding to one phonon. In borate, phonon energies can reach higher values (up to 1500 cm^{-1} [13]) so it can be assumed that in the oxyborate $Li_2Lu_5O_4(BO_3)_3$, one or two phonons are sufficient to compensate this difference (Fig.4).

2.2 $Yb^{3+} \rightarrow Eu^{3+}$ energy transfer

An $Yb^{3+} \rightarrow Eu^{3+}$ energy transfer by upconversion was also observed. Because the Yb^{3+} luminescence is less affected by cross-relaxation processes than the europium ion for a same array, larger amount of this ion can be introduced before reaching the concentration quenching treshold; this increases, for instance, the IR-visible conversion quantum efficiency of erbium and thulium [14,15].

W. Strek et al. reported an $Yb^{3+} \rightarrow Eu^{3+}$ energy transfer in a crystal of composition $KYb_{0.8}Eu_{0.2}(WO_4)_2$ [16], G.S. Maciel et al. Have observed this phenomenon in an Yb-Eu co-doped sol-gel processed silica glasses [17]. The first authors have proposed two mechanisms to explain this transfer:

(i) First, the energy of two ytterbium atoms in the excited state is transferred on the $^5D_2$ excited level of Eu^{3+}. Then the $^5D_2$ and $^5D_1$ levels relax non-radiatively to $^5D_0$ from which luminescence is observed. This process needs the simultaneous absorption of two photons. F.W. Ostermayer and L.G. van Uitert (1970) also described the cooperative sensitization of ytterbium cations and the energy transfer to a third acceptor in co-doped Yb, Tb-YF_3 [18].

(ii) The second mechanism is based on the [$^2F_{5/2}$-$^2F_{5/2}$] pair whose energy is equal to about 22000 cm^{-1}. The emission of a photon can occur from the simultaneous relaxation of the two excited ytterbium ions of a pair. This phenomenon explains the green emission of the $YbPO_4$ compound (λ_{exc}= 1 μm) [19]. This is a cooperative luminescence process and it allows energy transfer to the trivalent europium $^5D_2$ excited level in the case of the Yb-Eu co-doped compound.

Irradiation of the compound $Li_2Lu_5O_4(BO_3)_3$:Yb^{3+} 1%, Eu^{3+} x% (x=0.25, 1 molar substitution) by an AOC laser diode (spectral bandwidth from 2 to 4 nm at λ_{exc}= 973 nm) results in the visible emission of trivalent europium. The spectral distribution of the emission lines (Fig.7) is the same than that obtained for an excitation in the 4f→4f absorption lines of trivalent europium (λ_{exc}=394 nm). The global emission intensity increases with the square of the power of the incident beam (Fig.7). While exciting the compound $Li_2Lu_5O_4(BO_3)_3$:Yb^{3+} 1%, Eu^{3+} 1% by the AOC laser diode at 973 nm, we did not notice any blue cooperative luminescence of Yb^{3+}. This might be due to the weak Yb^{3+} concentration in this sample. So we can conclude in favor of the first mechanism with a cooperative sensitization to explain the Yb^{3+}→Eu^{3+} energy transfer. Similar tests were performed on an Eu^{3+} doped $Li_2Yb_5O_4(BO_3)_3$ compound but in this case, no red luminescence was detected showing the high probability of the Eu^{3+} → Yb^{3+} energy transfer versus the Yb^{3+}→Eu^{3+} cooperative energy transfer.

Conclusion

These studies performed on the $Li_2Lu_5O_4(BO_3)_3$ phase has led to the observation of a charge transfer emission of the ytterbium ion for the first time in a borate compound. This emission is located from the UV to the visible range. The $Tq_{50\%}$ is equal to 120 K. The optical characteristics as the Stokes shift and the lifetime are in agreement with those reported in the literature for the oxide Y_2O_3. Similar results have been obtained for the oxide Lu_2O_3.

Due to a cross-relaxation process between the $^5D_0$→$^7F_6$ Eu^{3+} levels and the $^2F_{7/2}$→$^2F_{5/2}$ Yb^{3+} levels, the luminescence of trivalent europium can only be observed in the lutetium phase and is quenched in the ytterbium one. Excitation in the ytterbium charge transfer states or in the europium absorption bands and lines leads to an infrared emission of the ytterbium ion in the Yb-Eu co-doped compound.

The luminescence of Eu^{3+} in the visible range can either be obtain for a conventional excitation in the europium absorption bands or lines or by an upconversion process allowing the $Yb^{3+} \rightarrow Eu^{3+}$ energy transfer by cooperative sensitization for an excitation in the 4f-4f ytterbium levels in the IR range in the lutetium co-doped samples.

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Figures captions

Figure 1. Normalized emission (a) and excitation (b) spectra of $Li_2Lu_{4.95}Yb_{0.05}O_4(BO_3)_3$ at 6K and variation of the integrated emission as a function of the temperature (black circle).

Figure 2. Normalized emission (a) and excitation (b) spectra of $Lu_{1.98}Yb_{0.02}O_3$ at 6K.

Figure 3. Normalized infrared emission of $Li_2Lu_{4.95}Yb_{0.05}O_4(BO_3)_3$ at 300K for an excitation at 230nm.

Figure 4. $Eu^{3+} \rightarrow Yb^{3+}$ energy transfer mechanism by cross-relaxation.

Figure 5 Normalized excitation spectra of the doped $Li_2Lu_5O_4(BO_3)_3$ phase associated with the different UV, visible and IR emissions:

a) $Li_2Lu_{4.95}Yb_{0.05}O_4(BO_3)_3$ (λ_{em}=345 nm) at 6 K

b) $Li_2Lu_{4.9375}Yb_{0.05}Eu_{0.0125}O_4(BO_3)_3$ (λ_{em}=973 nm) at 300 K

c) $Li_2Lu_{4.9}Yb_{0.05}Eu_{0.05}O_4(BO_3)_3$ (λ_{em}=973 nm) at 300 K

d) $Li_2Lu_{4.9}Yb_{0.05}Eu_{0.05}O_4(BO_3)_3$ (λ_{em}=609 nm) at 300 K

Figure 6 Infrared emission spectra of $Li_2Lu_{4.95-x}Yb_{0.05}Eu_xO_4(BO_3)_3$ [a) x= 0. b) x= 0.0125. c) x= 0.05], for excitation at 285 nm.

Figure 7 Normalized visible emission spectra of $Li_2Lu_{4.9}Yb_{0.05}Eu_{0.05}O_4(BO_3)_3$, for excitations at 394 nm (xenon lamp source, dotted line) and at 973 nm (laser diode, full line) at 300K and variation of the integrated intensity as function as the diode power (black circles).

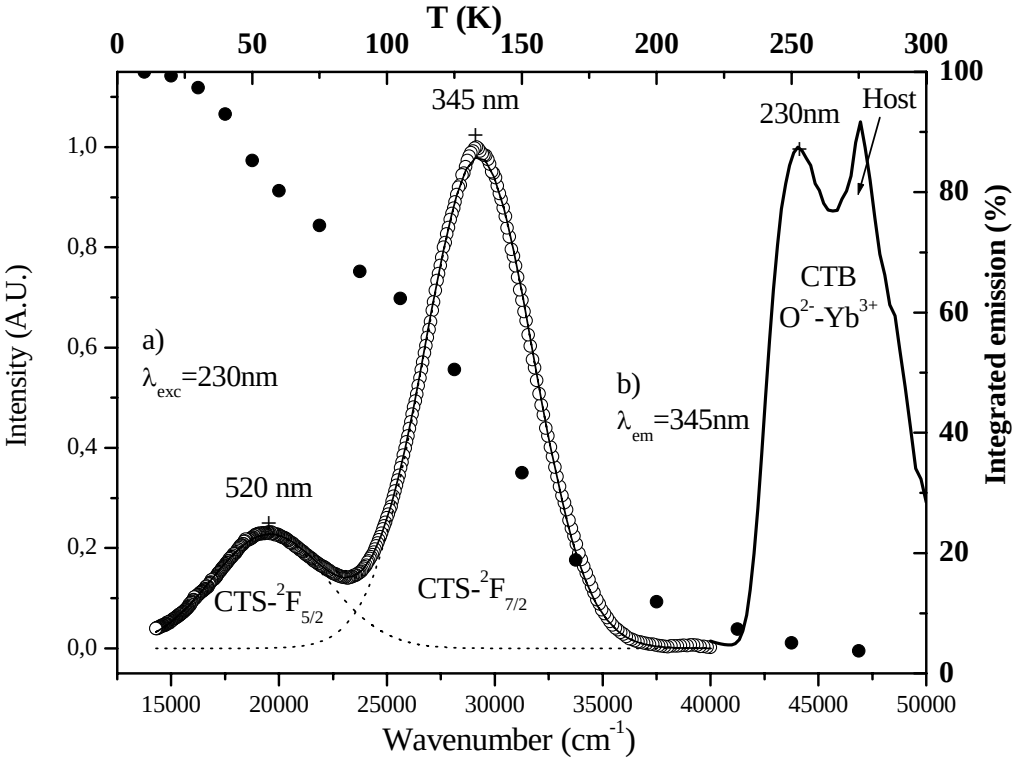
T (K)
0
50
100
150
200
250
300
100
80
60
40
20
0
Integrated emission (%)
345 nm
230nm
Host
CTB
O2--Yb3+
a)
λexc=230nm
b)
λem=345nm
520 nm
CTS-2F5/2
CTS-2F7/2
1,0
0,8
0,6
0,4
0,2
0,0
Intensity (A.U.)
15000
20000
25000
30000
35000
40000
45000
50000
Wavenumber (cm-1)

Figure 1.

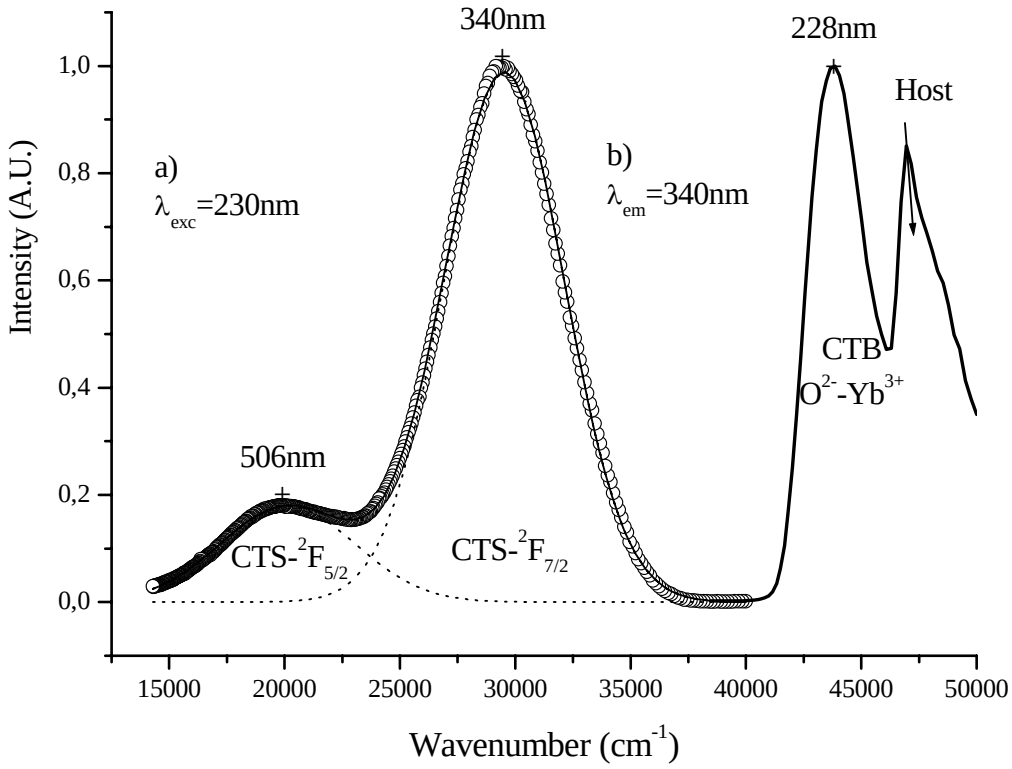
340nm
228nm
Host
a)
λexc=230nm
b)
λem=340nm
CTB
O2--Yb3+
506nm
CTS-2F5/2
CTS-2F7/2
Intensity (A.U.)
Wavenumber (cm-1)
1,0
0,8
0,6
0,4
0,2
0,0
15000
20000
25000
30000
35000
40000
45000
50000

Figure 2.

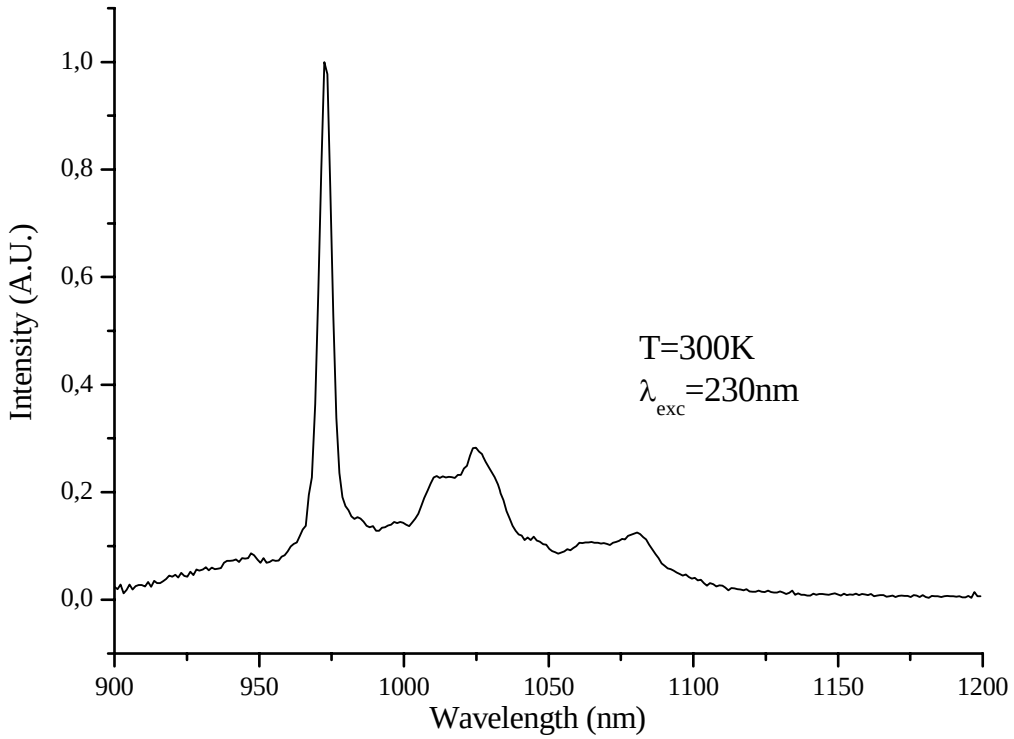
1,0
0,8
0,6
0,4
0,2
0,0
Intensity (A.U.)
T=300K
λexc=230nm
900
950
1000
1050
1100
1150
1200
Wavelength (nm)

Figure 3.

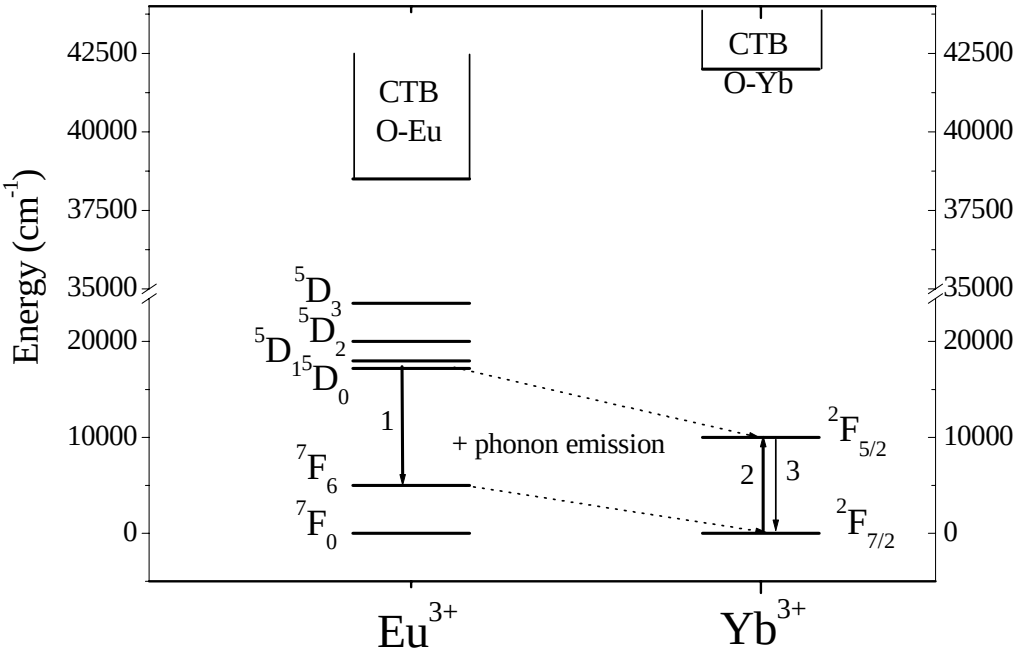
Energy (cm-1)
42500
40000
37500
35000
20000
10000
0
CTB
O-Eu
CTB
O-Yb
5D3
5D2
5D1
5D0
7F6
7F0
1
+ phonon emission
2
3
2F5/2
2F7/2
Eu3+
Yb3+

Figure 4.

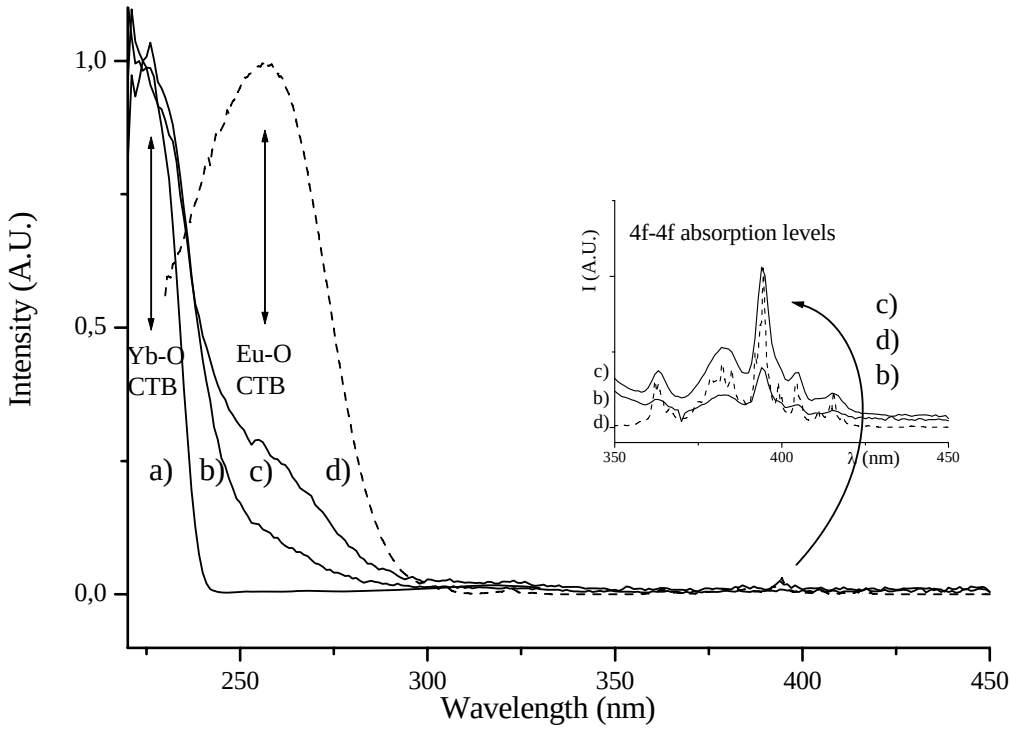
1,0
0,5
0,0
Intensity (A.U.)
Yb-O
CTB
Eu-O
CTB
a)
b)
c)
d)
4f-4f absorption levels
I (A.U.)
c)
b)
d)
350
400
λ (nm)
450
c)
d)
b)
250
300
350
400
450
Wavelength (nm)

Figure 5.

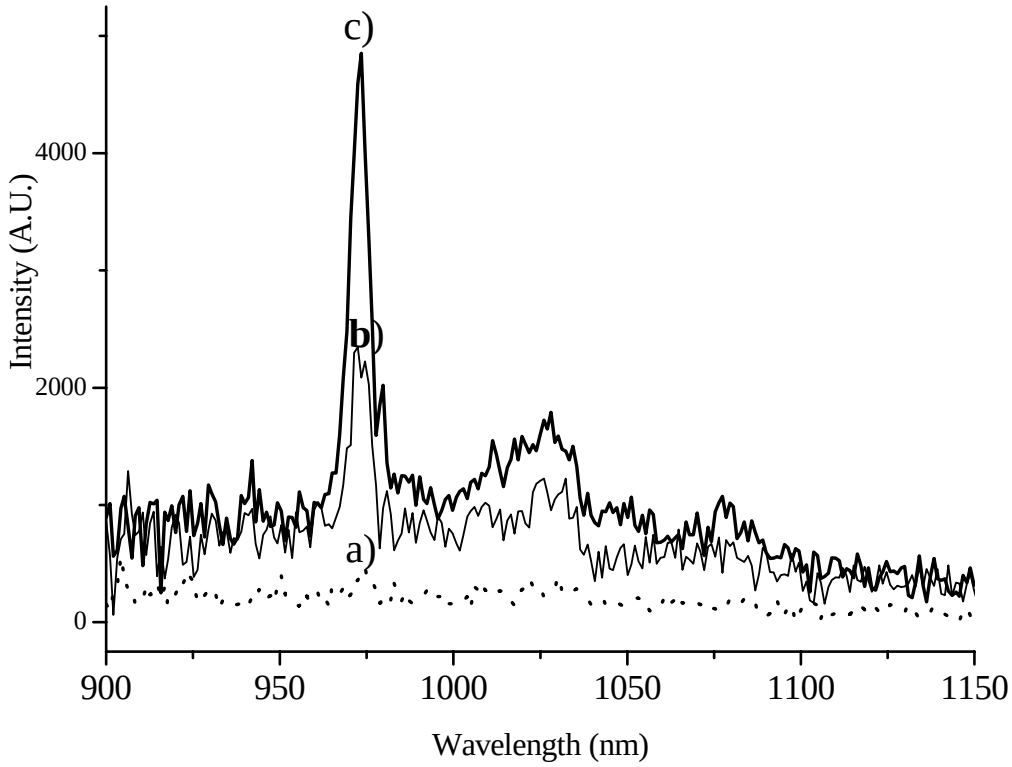
c)
b)
a)
4000
2000
0
Intensity (A.U.)
900
950
1000
1050
1100
1150
Wavelength (nm)

Figure 6.

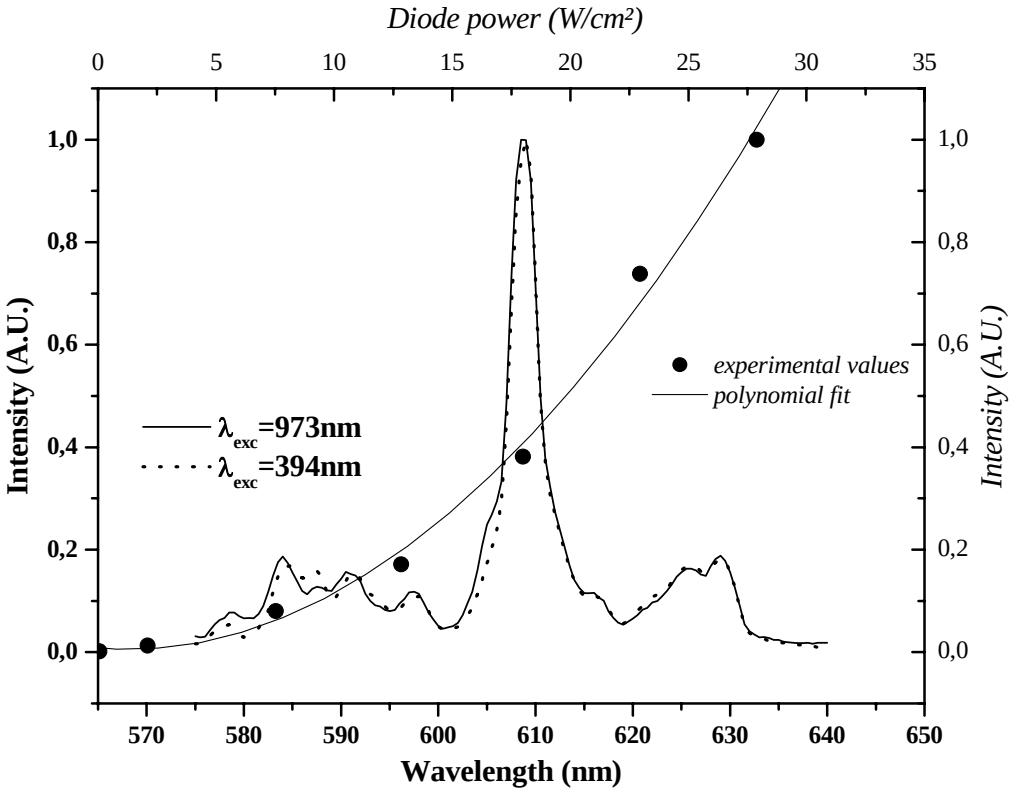
Diode power (W/cm²)
0
5
10
15
20
25
30
35
1,0
0,8
0,6
0,4
0,2
0,0
Intensity (A.U.)
Intensity (A.U.)
experimental values
polynomial fit
λexc=973nm
λexc=394nm
570
580
590
600
610
620
630
640
650
Wavelength (nm)

Figure 7