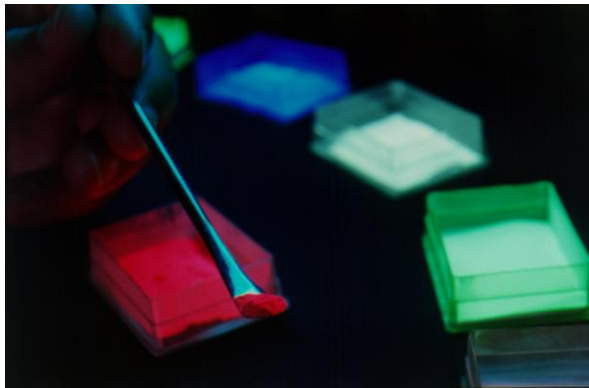


Luminescence des terres rares et aspects structuraux au sein de composés cristallisés



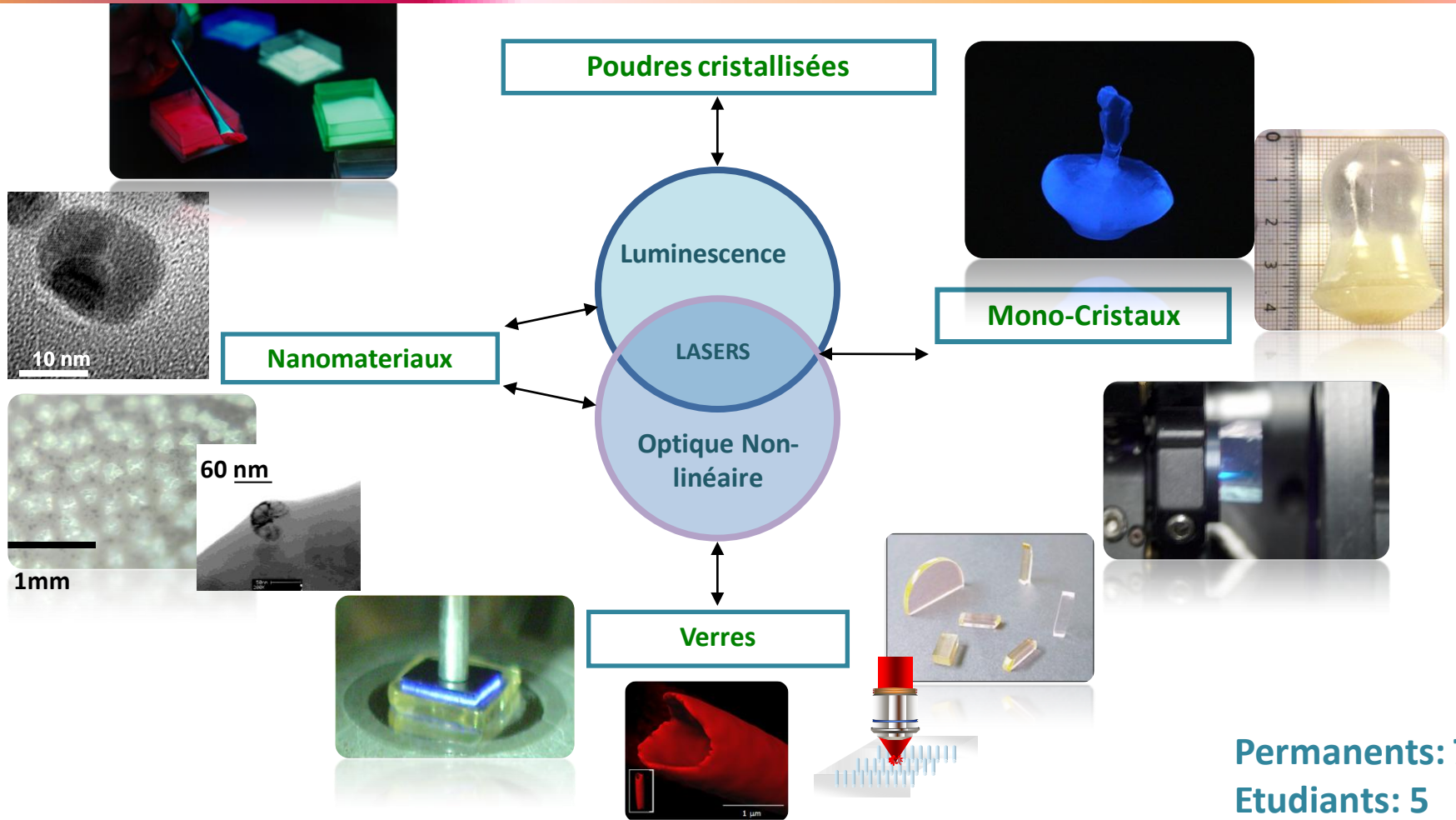
V. Jubera



GRUPE 3 MATERIAUX POUR L'OPTIQUE

Coordinateur : **Thierry Cardinal**

Chargé de Recherche



- Introduction
- Bandes ou raies: représentation des mécanismes de transitions
- Les sondes structurales
- Choix des longueurs d'onde d'excitation
- Effet de concentration
- Champ cristallin et localisation des ions dopants

Introduction

La	* 58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0				
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 18.00	10 Ne 20.18	Y
11 Na 22.99	12 Mg 24.31	IIIB	IVB	VB	VIB	VII B	VIII B			IB	II B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95	Sc
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3	
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra (226.0)	89 Ac (137)	104 Rf	105 Ha	106 Unh	107 Uns	108	109 Une										
Lanthanides		* 58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0			
		~ 90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)			

- Degré d'oxydation: +3 (Oxydes: **CeO₂**, **Pr₆O₁₁**, Nd₂O₃, Sm₂O₃, **Eu₂O₃**, Gd₂O₃, **Tb₄O₇**, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃)

Introduction

La	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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- Contraction lanthanidique

Elements	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Electronic configuration	4f ¹ 5d ⁰ 6s ²	4f ¹ 5d ¹ 6s ²	4f ² 6s ²	4f ³ 6s ²	4f ⁴ 6s ²	4f ⁵ 6s ²	4f ⁶ 6s ²	4f ⁷ 5d ¹ 6s ²	4f ⁹ 6s ²	4f ¹⁰ 6s ²	4f ¹¹ 6s ²	4f ¹² 6s ²	4f ¹³ 6s ²	4f ¹⁴ 6s ²	4f ¹⁴ 5d ¹ 6s ²
Ln ³⁺ electr. Conf.	4f ⁰	4f ¹	4f ²	4f ³	4f ⁴	4f ⁵	4f ⁶	4f ⁷	4f ⁸	4f ⁹	4f ¹⁰	4f ¹¹	4f ¹²	4f ¹³	4f ¹⁴
Ln ³⁺ Radius (pm) Coord 6	117	102	99	98.3	97	95.8	94.7	93.8	92.3	91.2	90.1	89	88	86.8	86.1

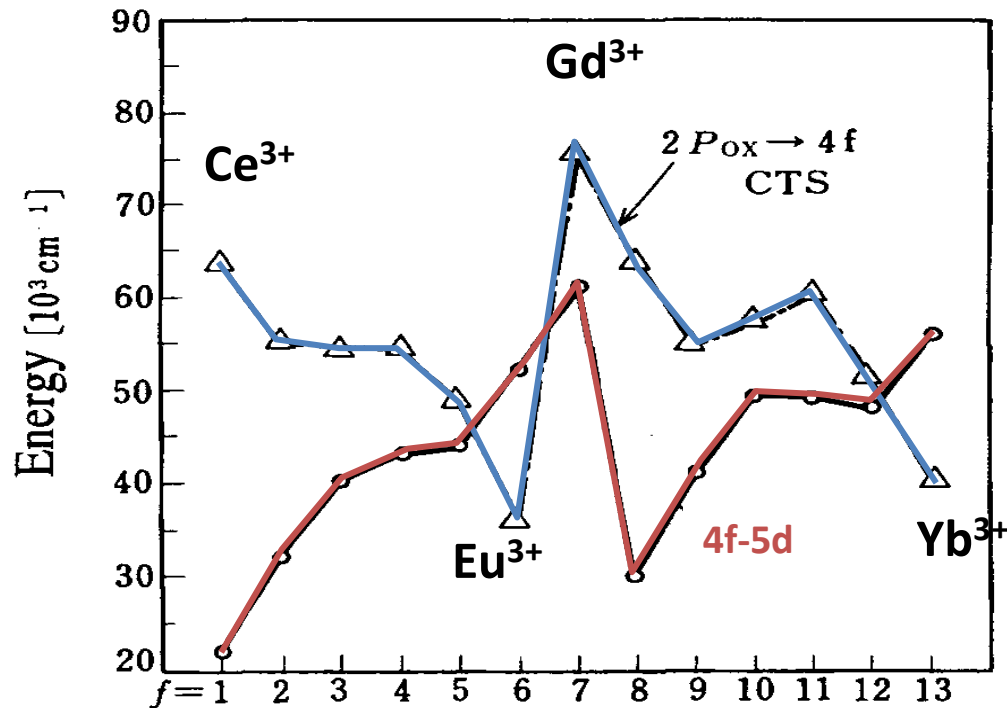


Coordination de 7 à 12

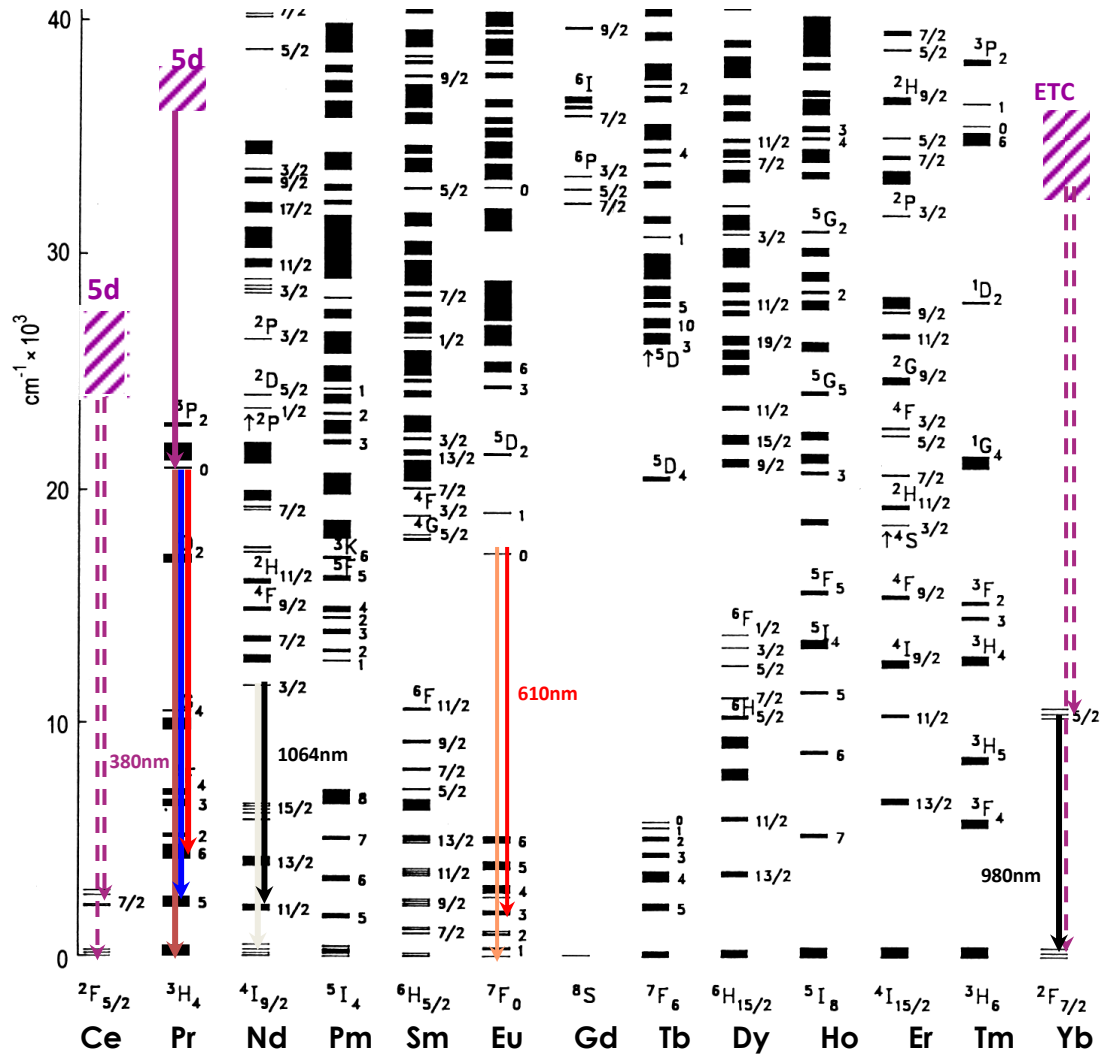
Introduction

La	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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Variation des énergies entre 4f-5d ou BTC



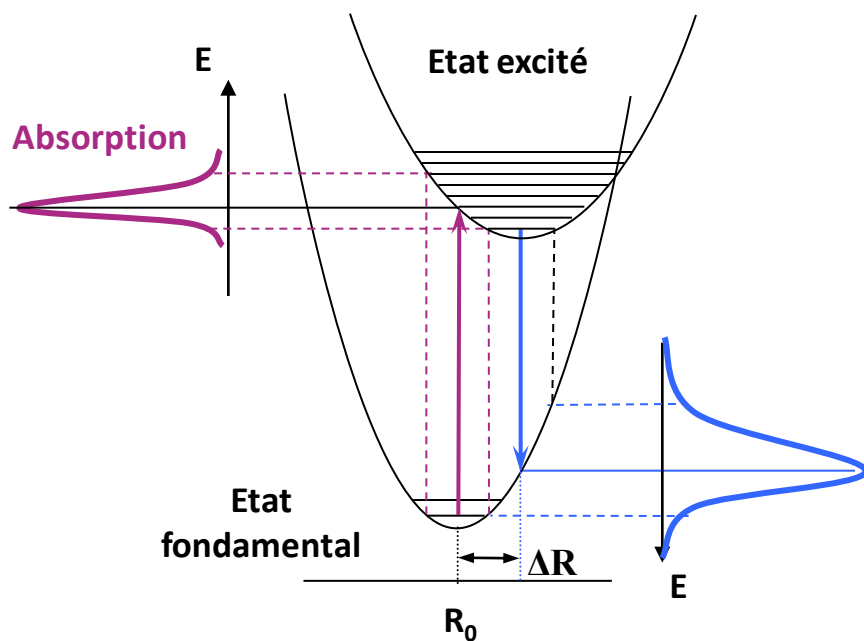
Introduction



Bandes ou raies: représentation des mécanismes de transition

Transitions

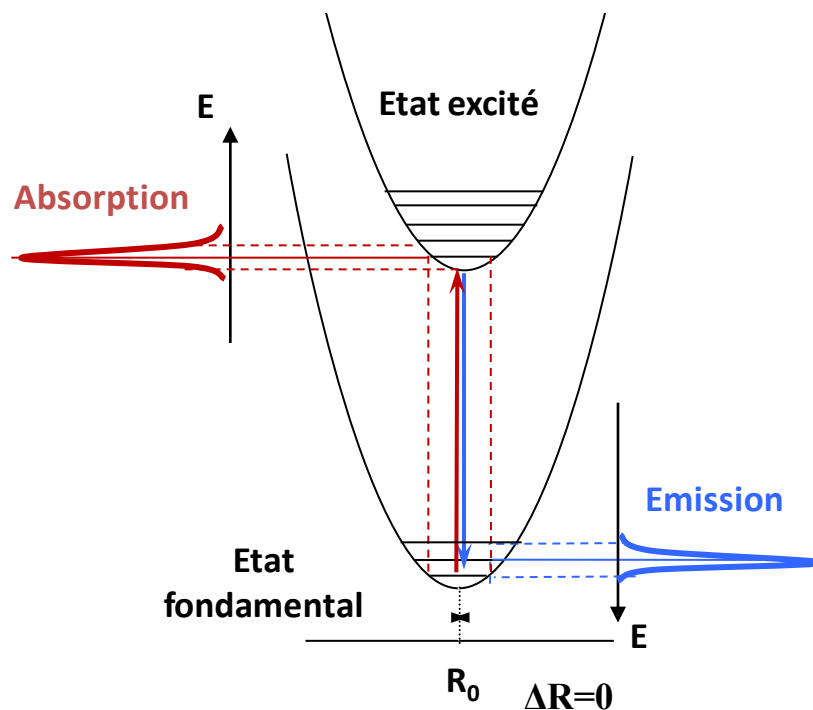
5d-4f ou ETC-4f



Spectre de bandes

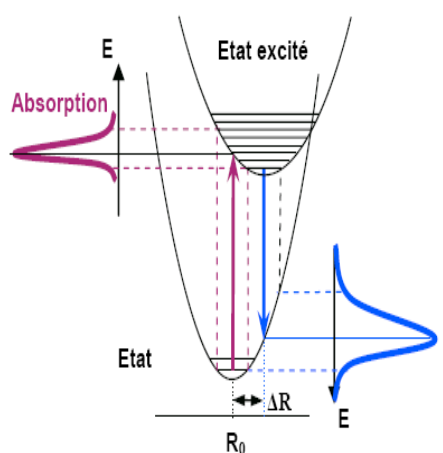
Transitions

4f-4f

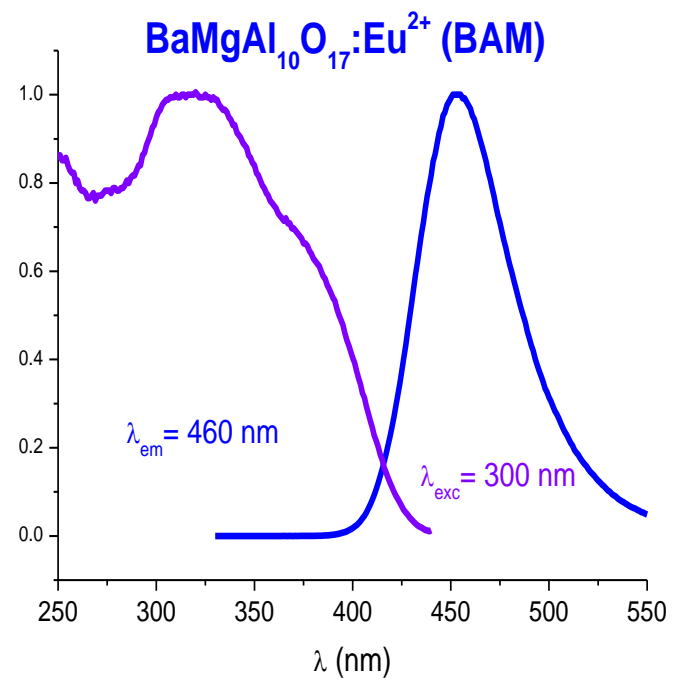
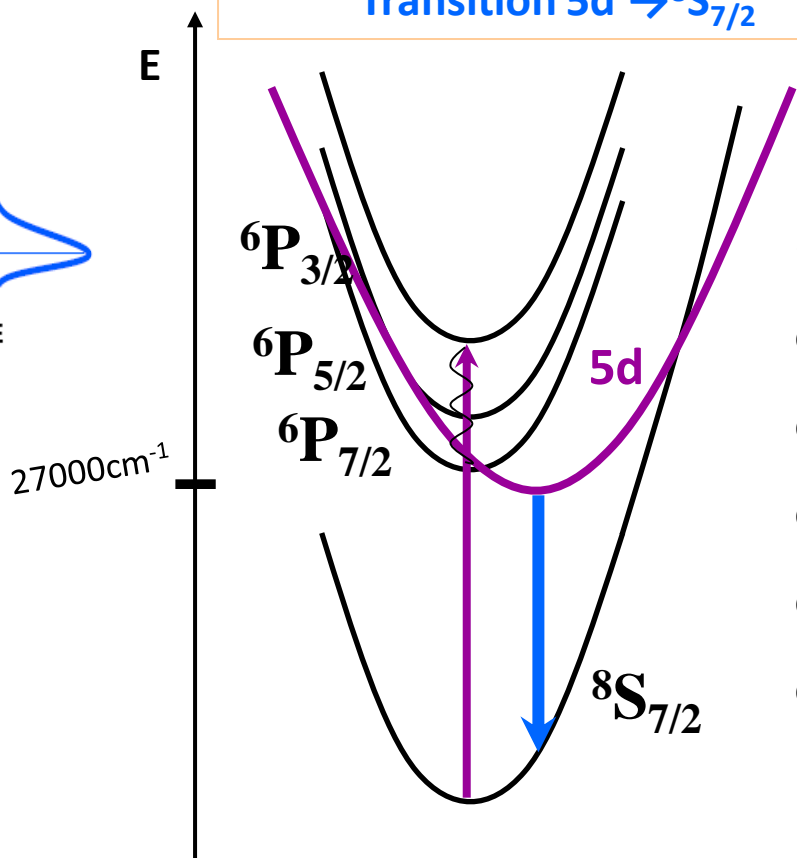


Spectre de raies

Bandes ou raies: représentation des mécanismes de transition



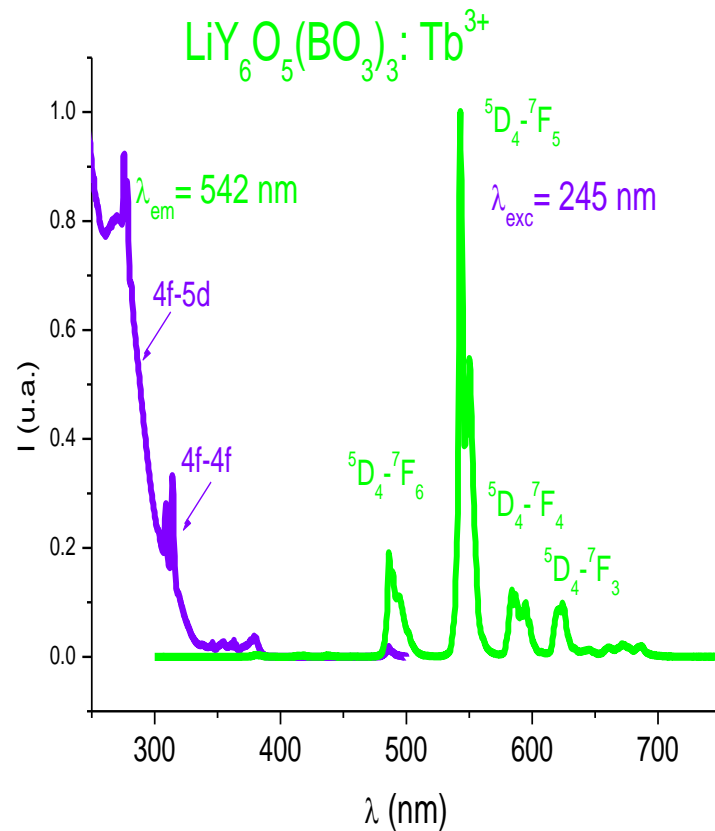
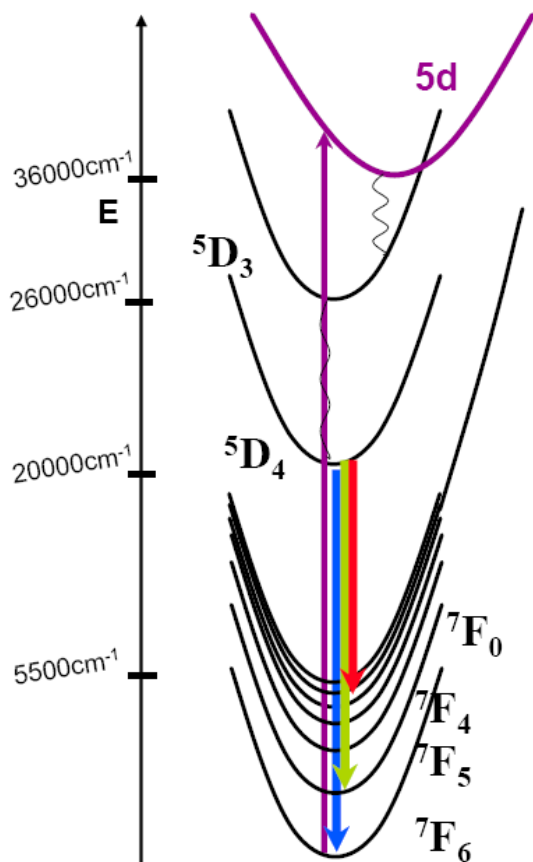
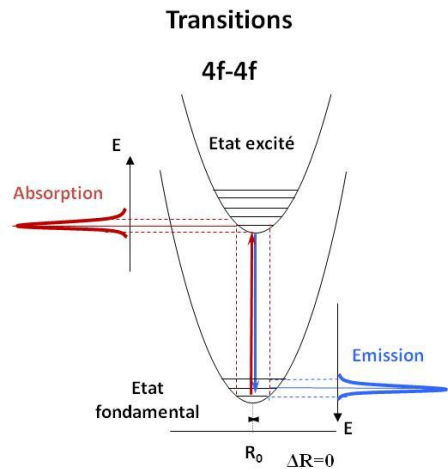
Eu²⁺ 4f⁷
Transition 5d → ⁸S_{7/2}



Spectre de bandes

Bandes ou raies: représentation des mécanismes de transition

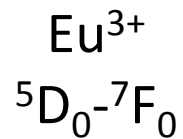
Tb³⁺ 4f⁸
Transition ⁵D₄ → ⁷F_J



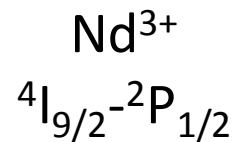
Spectre de raies

Les sondes structurales

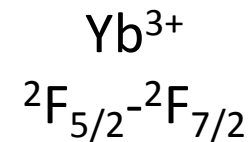
- nombre de sites
- nature du site
- occupation du site
- levée de dégénérescence des niveaux



Emission
Visible

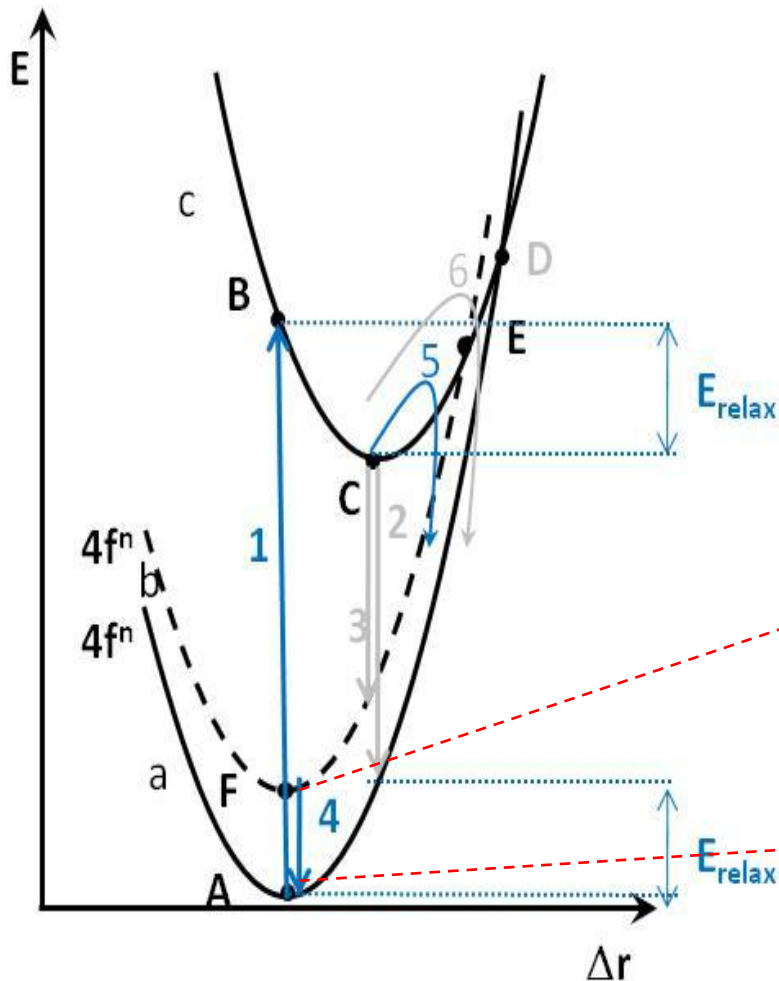


Absorption
UV



Absorption
Emission
IR

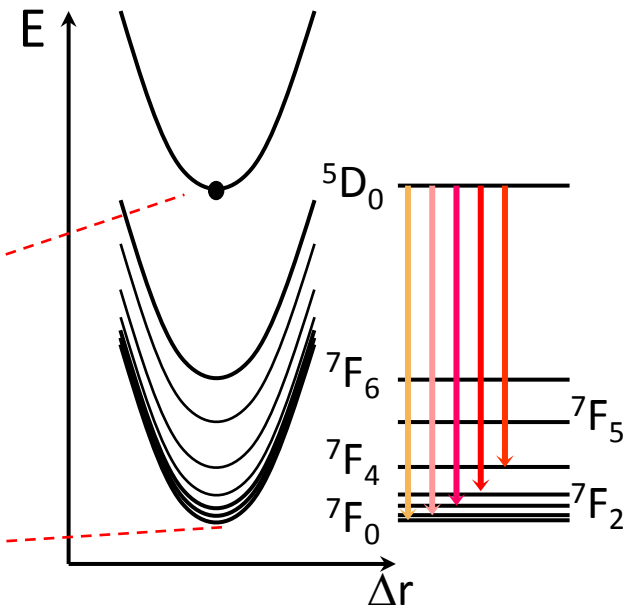
Désexcitation depuis l'ETC sur les niveau 4f



Choix de l'ion: **Eu³⁺**

Choix des matrices:

borate, oxyborates ...



Eu³⁺

- Décompte du nombre de sites occupés par l'ion dopant:
 - Transition singulet –singulet 5D_0 - 7F_0
- Détermination de la symétrie du site
 - Ecart à la centro-symétrie:
Rapport 5D_0 - 7F_2 / 5D_0 - 7F_1
 - Groupe ponctuel de symétrie
Eclatement des niveaux sous l'effet
du champ cristallin

Les sondes structurales

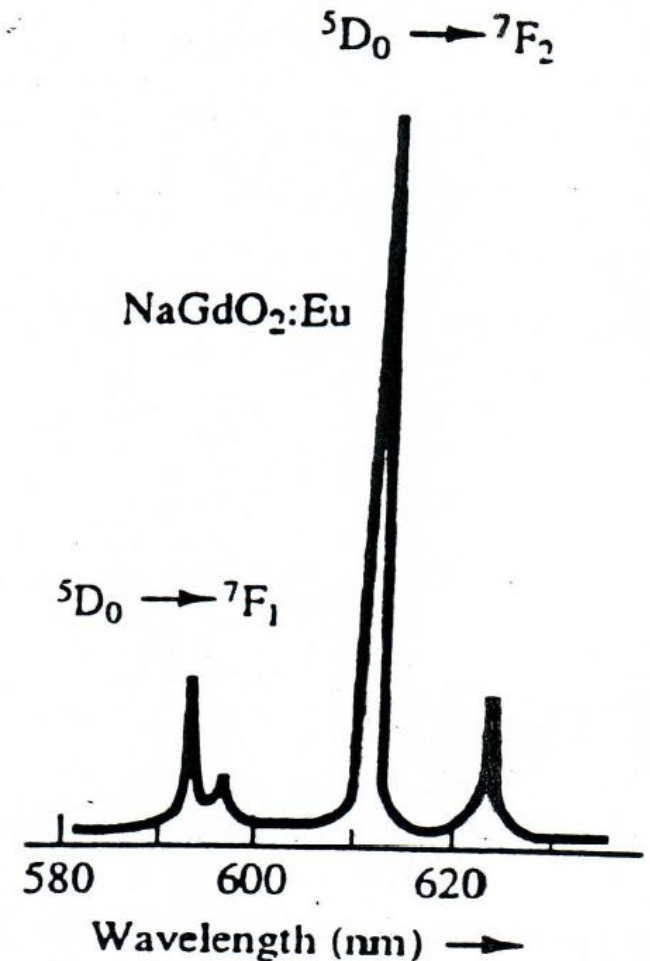
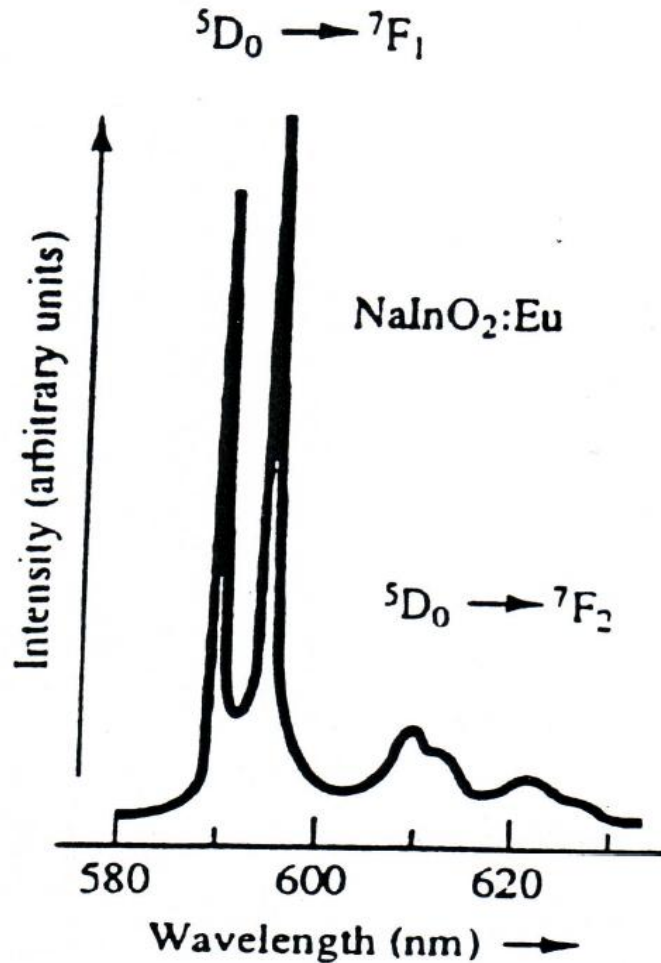
Eu³⁺

Détermination de la symétrie: site centro/non centro

Rapport

$$\frac{{}^5D_0 \rightarrow {}^7F_2}{{}^5D_0 \rightarrow {}^7F_1}$$

$$\frac{{}^5D_0 \rightarrow {}^7F_2}{{}^5D_0 \rightarrow {}^7F_1}$$



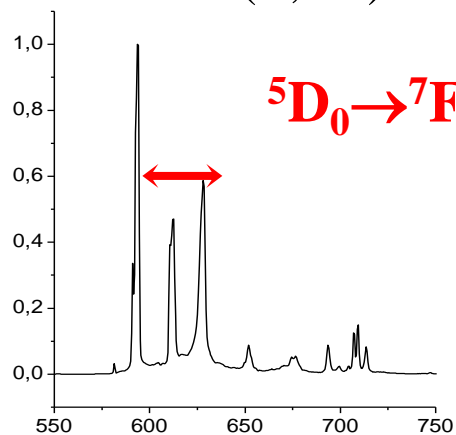
Les sondes structurales

Détermination de la symétrie: site centro/non centro

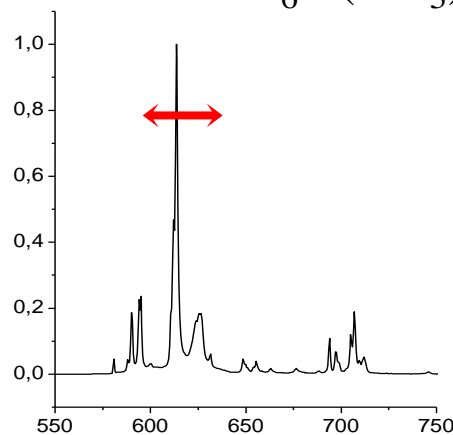
Eu³⁺

$\lambda_{exc} = 250 \text{ nm}$

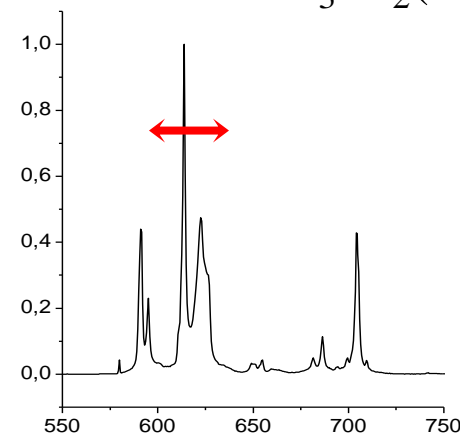
(Y,Gd)BO₃



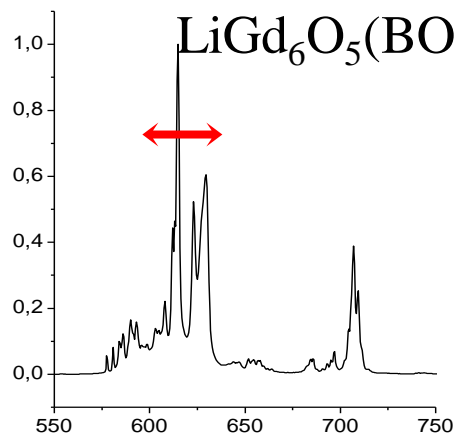
Li₆Y(BO₃)₃



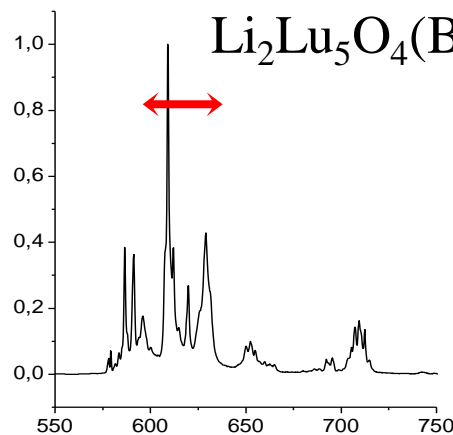
Li₃La₂(BO₃)₃



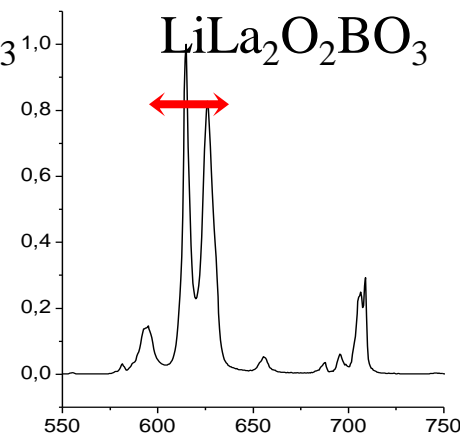
LiGd₆O₅(BO₃)₃



Li₂Lu₅O₄(BO₃)₃

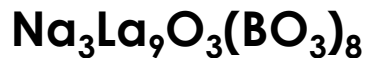


LiLa₂O₂BO₃



Les sondes structurales

Eu³⁺



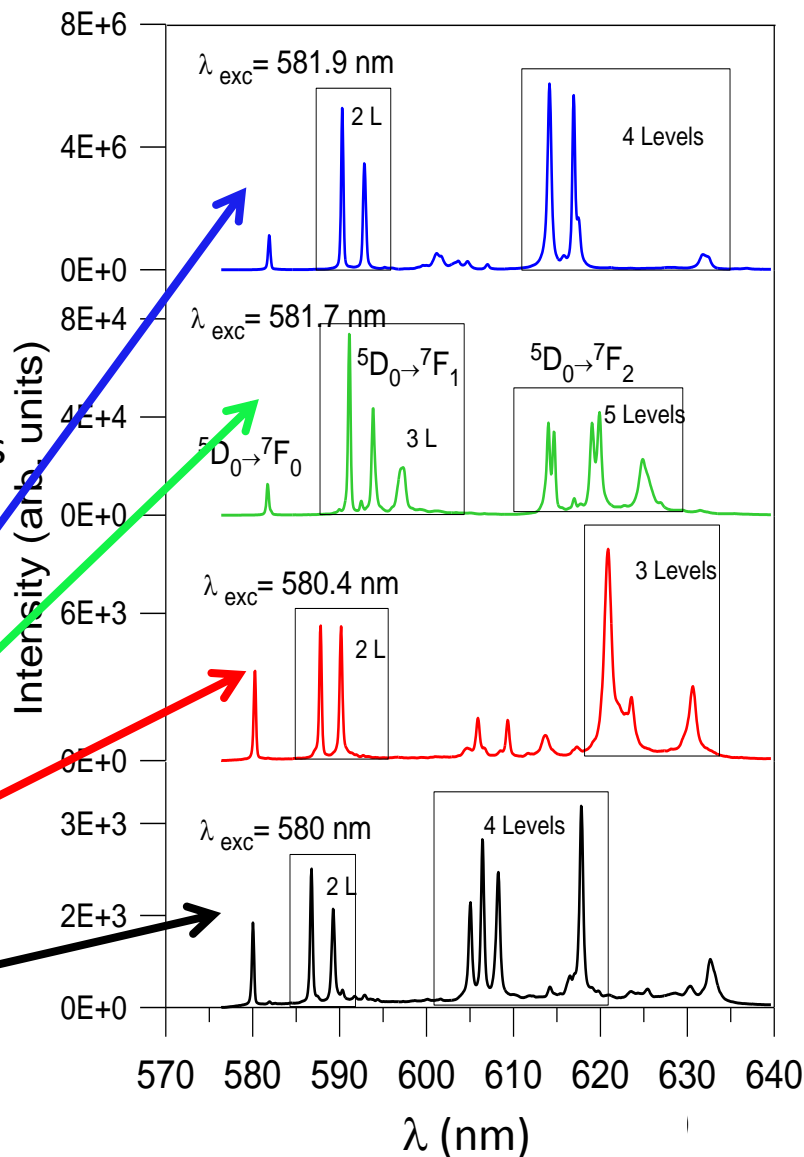
Maille hexagonale
Groupe d'espace: P-6 2 m
2 positions indépendantes pour Ln³⁺

LnO₈ site C_{4v}

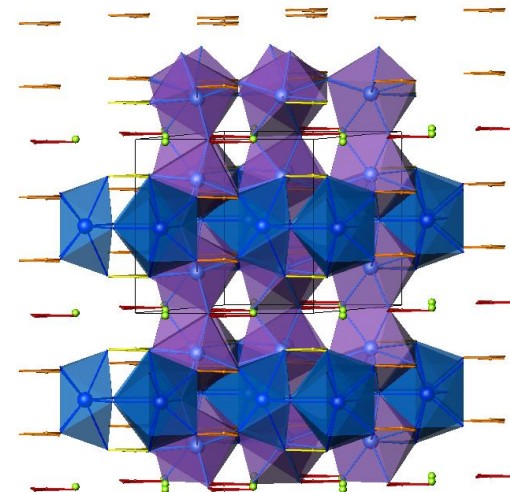
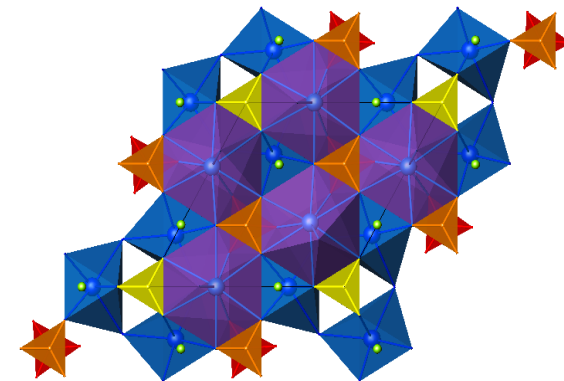
LnO₉ site C_{2v}

NaO₈ site C_{3v}

Défaut site C_{4v}



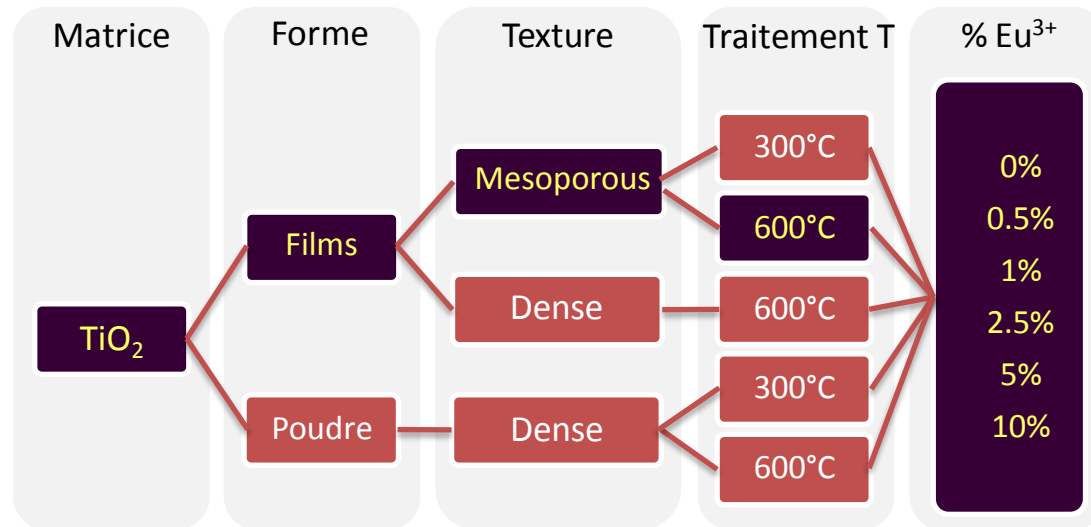
Projection selon le plan (b)



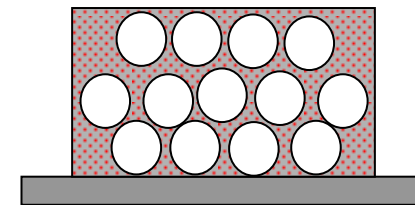
Les sondes structurales

TiO₂ (voies sol gel)

Voies de synthèse mises en œuvre



Propriétés de luminescence et localisation de la terre rare ?

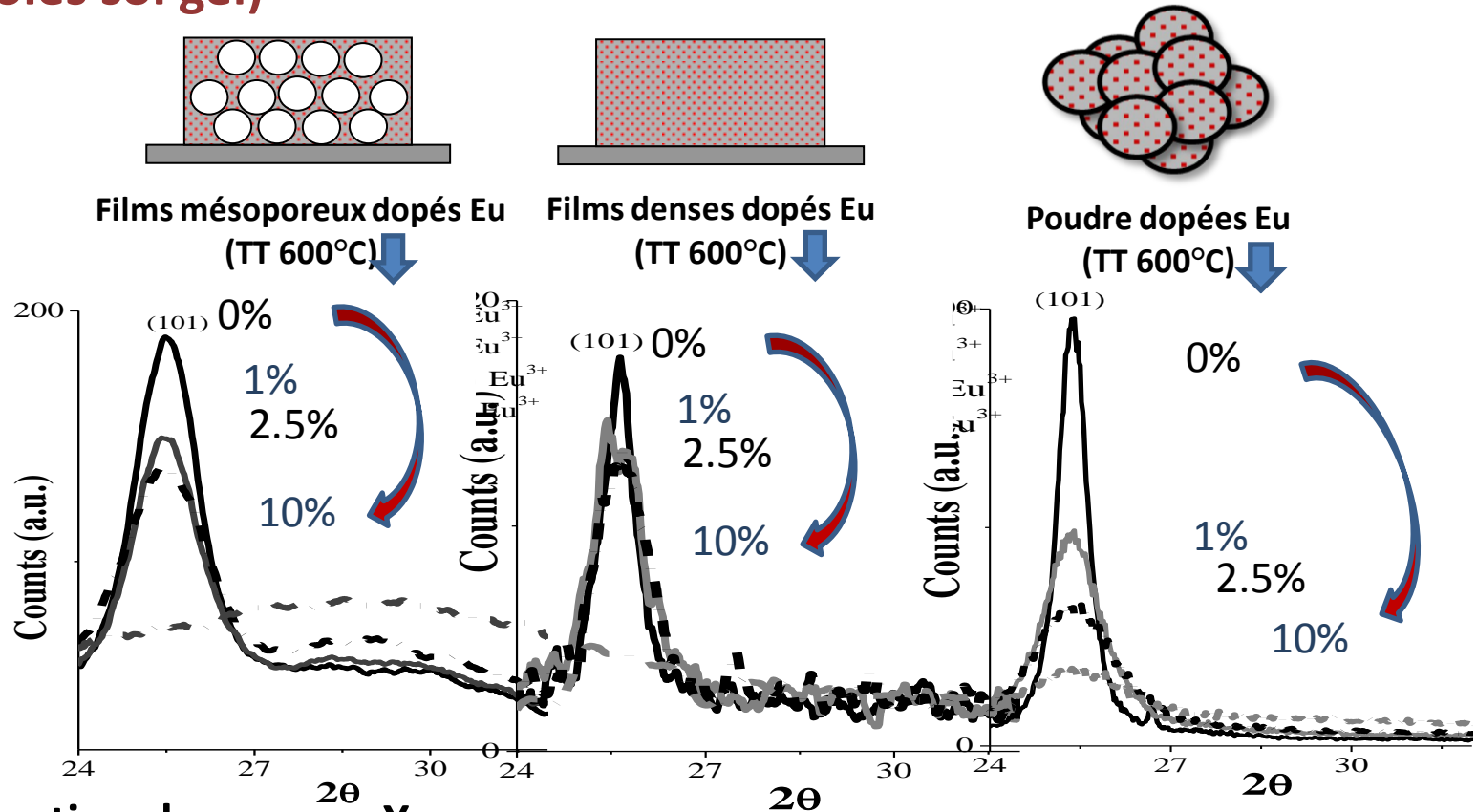


Films mésoporeux de TiO₂ dopés Eu

Les sondes structurales

TiO₂: effet de forme et de structure

TiO₂ (voies sol gel)



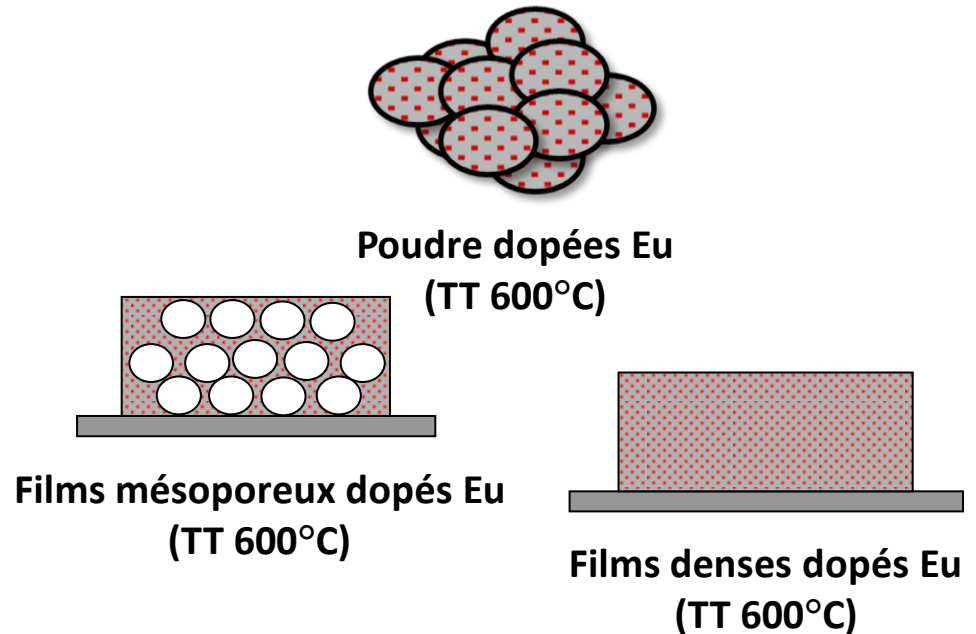
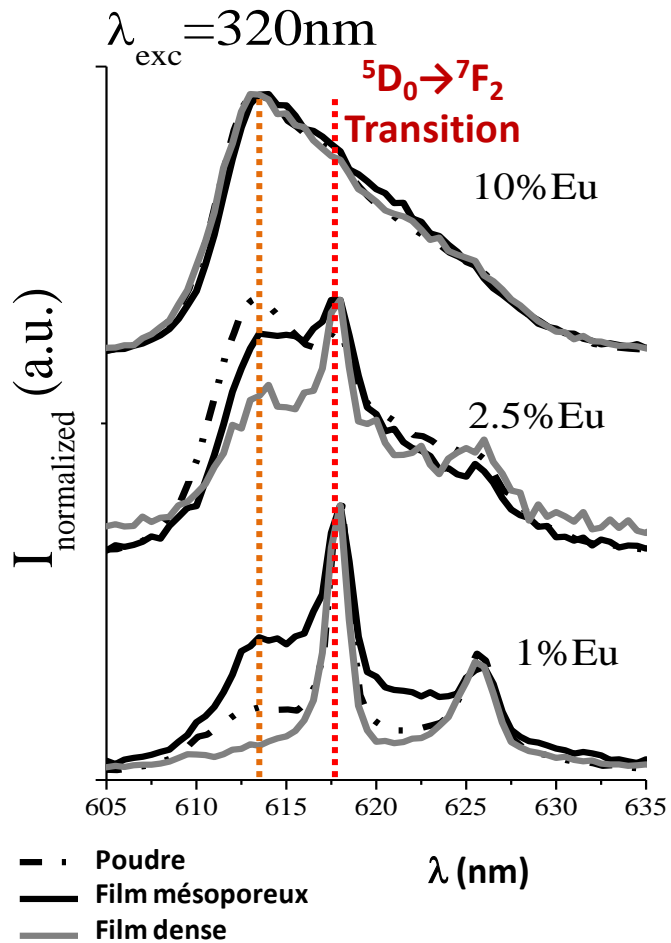
Diffraction des rayons X:

Retard de la cristallisation observé avec l'augmentation du taux en Eu³⁺

Effet plus prononcé sur les systèmes mésoporeux

TiO₂: effet de forme et de structure

TiO₂ (voies sol gel)

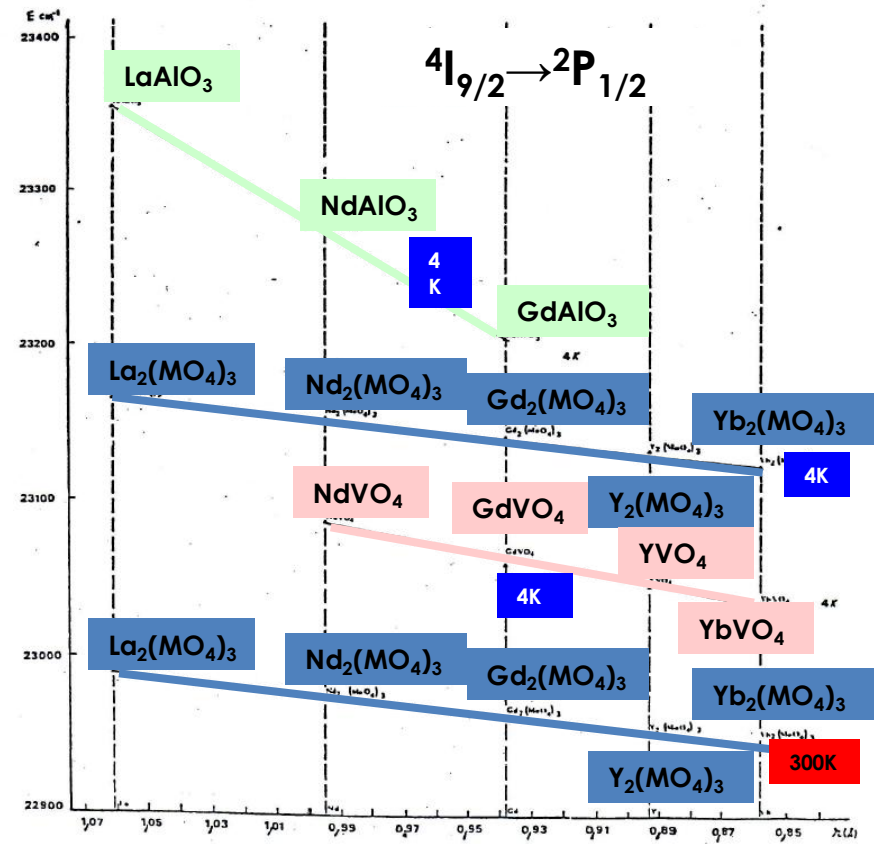
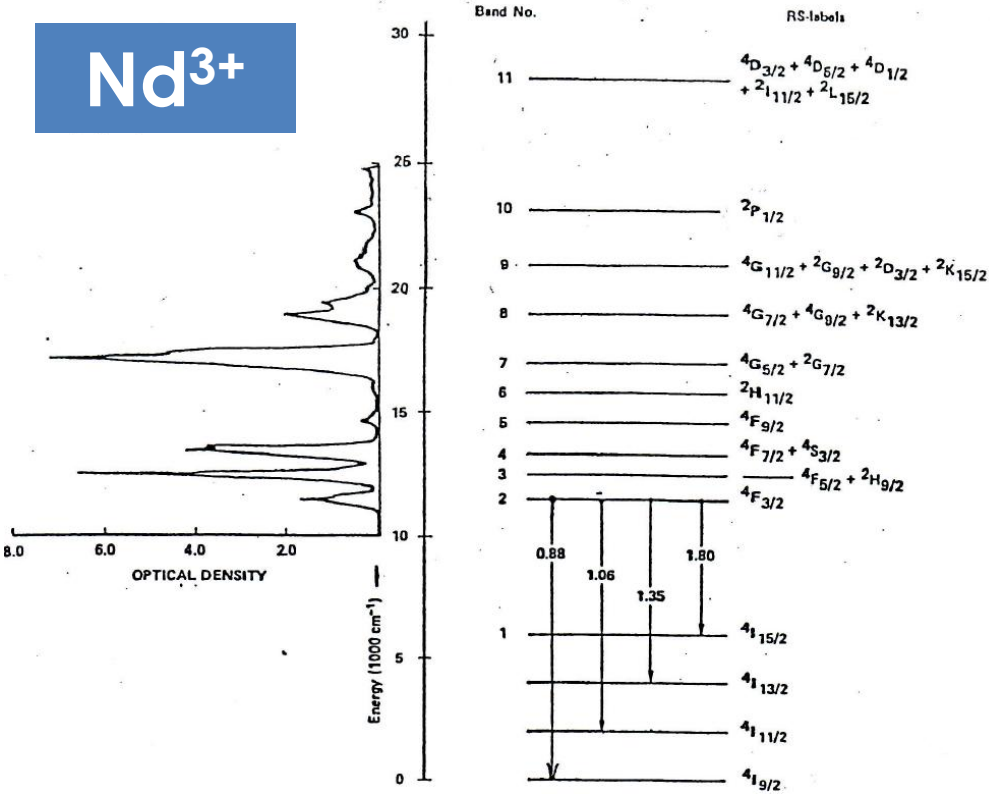


Luminescence

- Réponses similaires sur les trois systèmes avec le taux en Eu³⁺
- 1 composante amorphe
- 1 composante cristallisée

Les sondes structurales

Nd³⁺

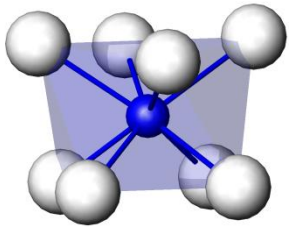


➔ Sonde structurale en absorption

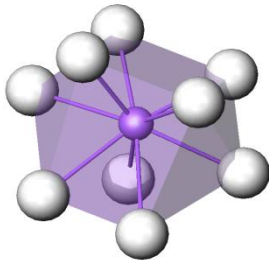
Les sondes structurales

Nd³⁺

Na₃La₉O₃(BO₃)₈ compound

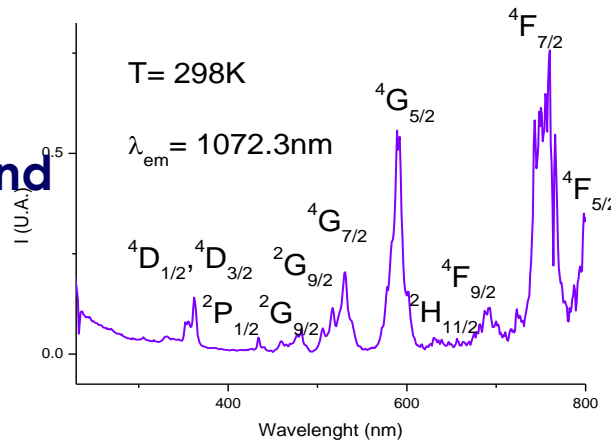


LaO₈

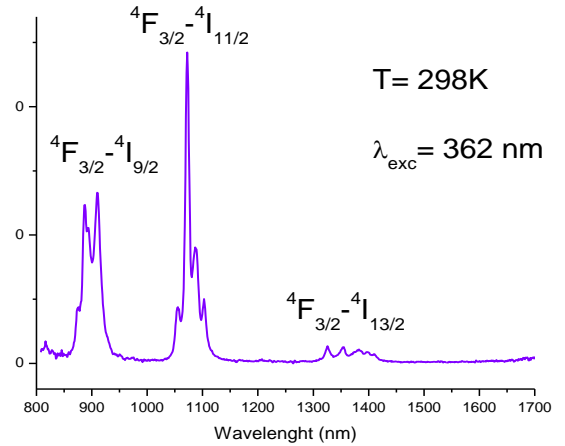


LaO₉

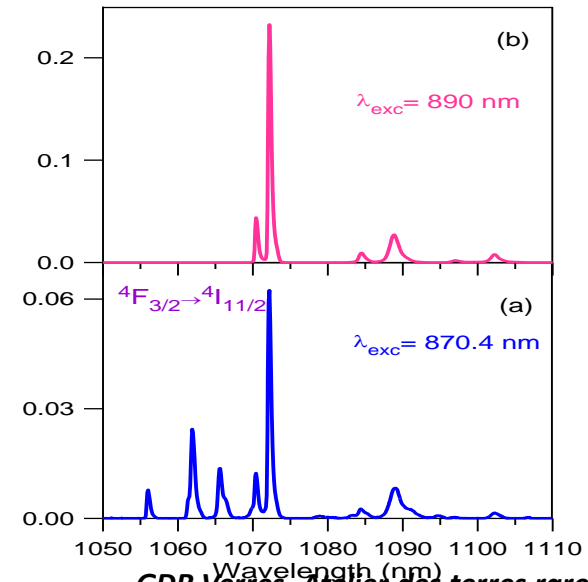
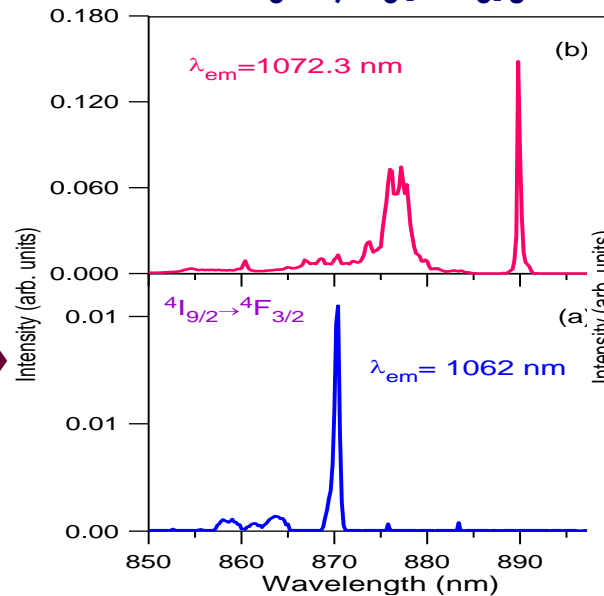
Excitation laser
sélective pour
observer les deux
environnements de
Nd³⁺ sur les sites du
La³⁺



Spectres d'excitation de Nd³⁺ (0.8%) au sein du cristal Na₃La₉O₃(BO₃)₈



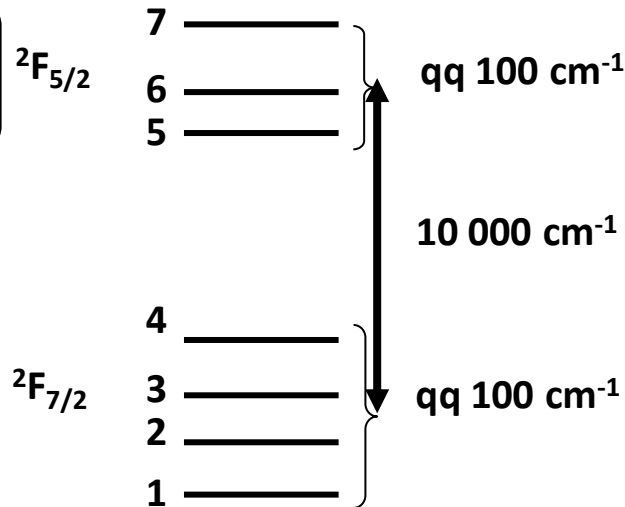
Spectres d'émission de Nd³⁺ (0.8%) au sein du cristal Na₃La₉O₃(BO₃)₈.



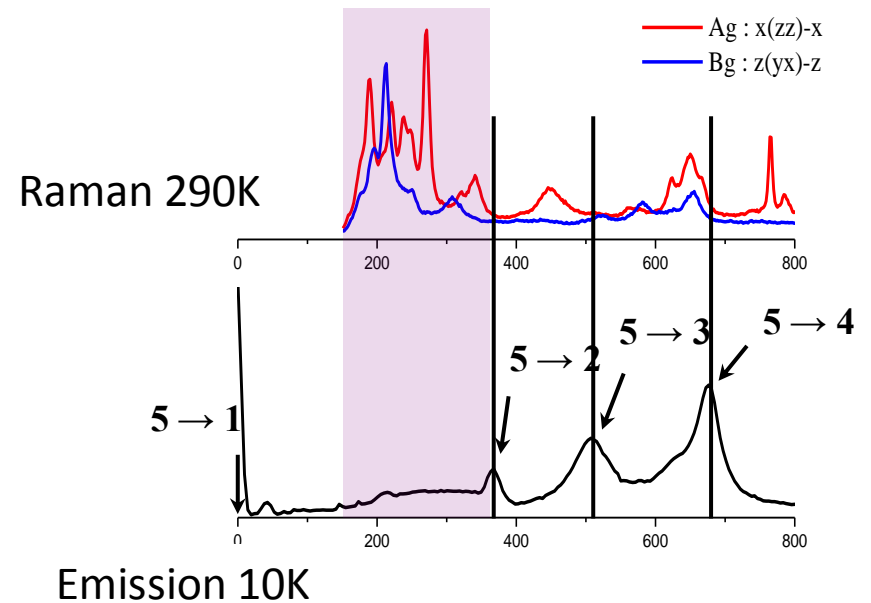
Les sondes structurales

Borate $\text{Li}_6\text{Ln}(\text{BO}_3)_3$: 1 site de substitution potentiel

Yb³⁺



Niveaux d'énergie de l'ion Yb^{3+} au sein du composé $\text{Li}_6\text{Gd}(\text{BO}_3)_3$



Identification des composantes Stark		Energie (cm ⁻¹)
$2F_{5/2}$	7	10834
	6	10488
	5	10290
$2F_{7/2}$	4	687
	3	515
	2	368
	1	0

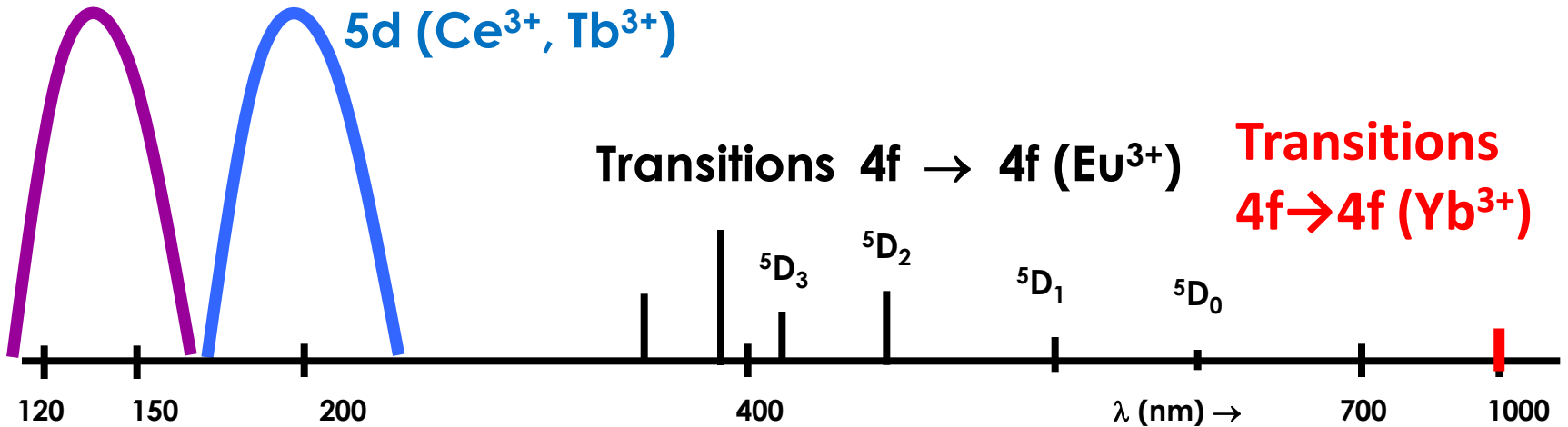
J. Sablayrolles, V. Jubera, F. Guillen, R. Decourt, M. Couzi, J.P. Chaminade, A. Garcia, Optics Commun., 280 (2007) 103

Choix des longueurs d'onde d'excitation

Réseau hôte

BTC (Eu^{3+} , Yb^{3+})

5d (Ce^{3+} , Tb^{3+})



Réseau hôte

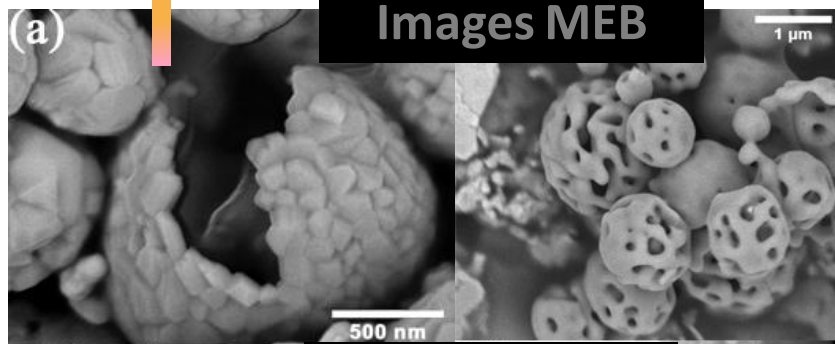
BV \rightarrow BC

BTC
 $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$
ligand
ou
 $4f \rightarrow 5d$ Ce^{3+} , Tb^{3+}
Forte absorption

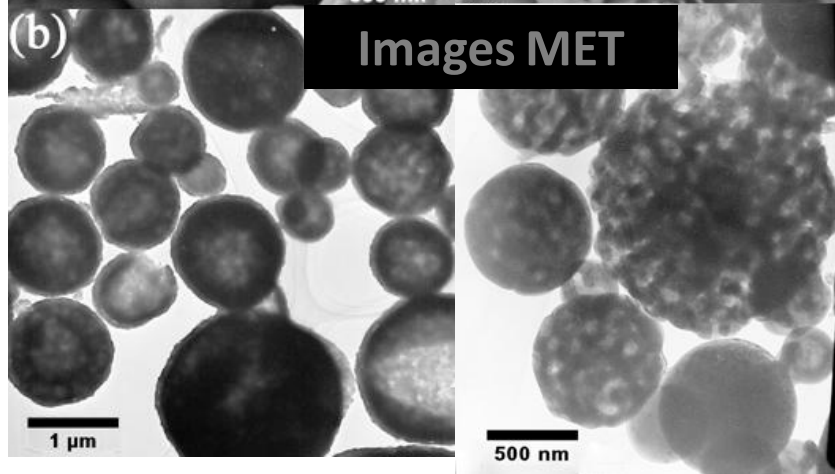
Transitions $4f^n \rightarrow 4f^n$
Transitions interdite:
faible absorption

Choix des longueurs d'onde d'excitation

Images MEB



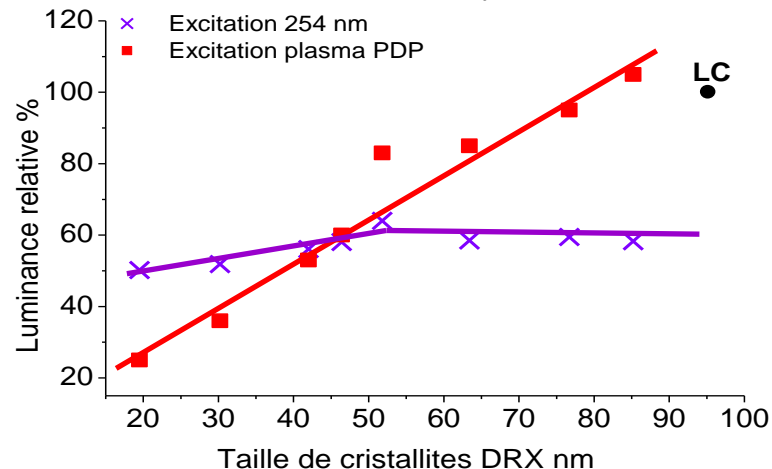
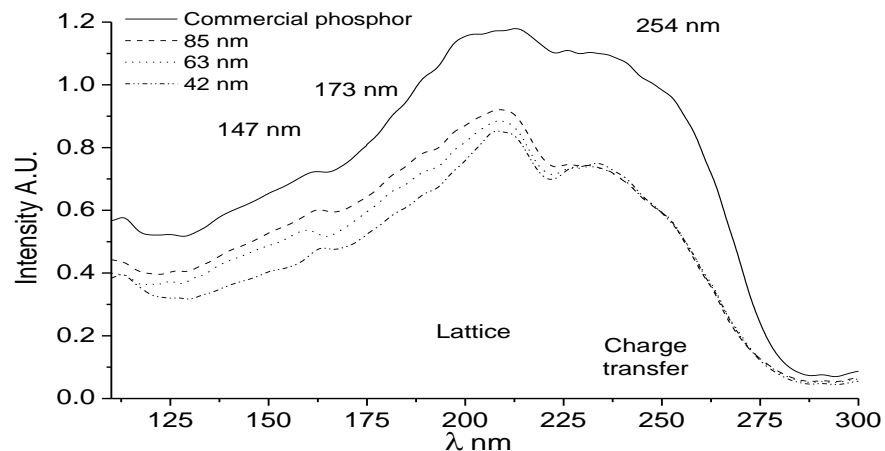
Images MET



Y₂O₃:Eu³⁺ 3,5%
Luminophore rouge

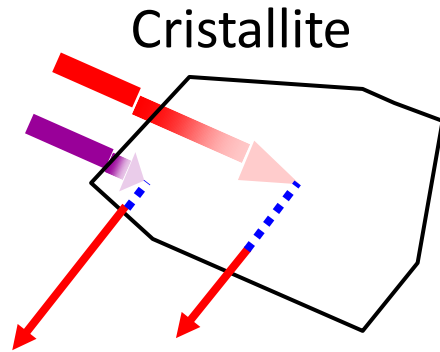
Sphères creuses
(épaisseur 100nm)

Synthèse par spray pyrolyse

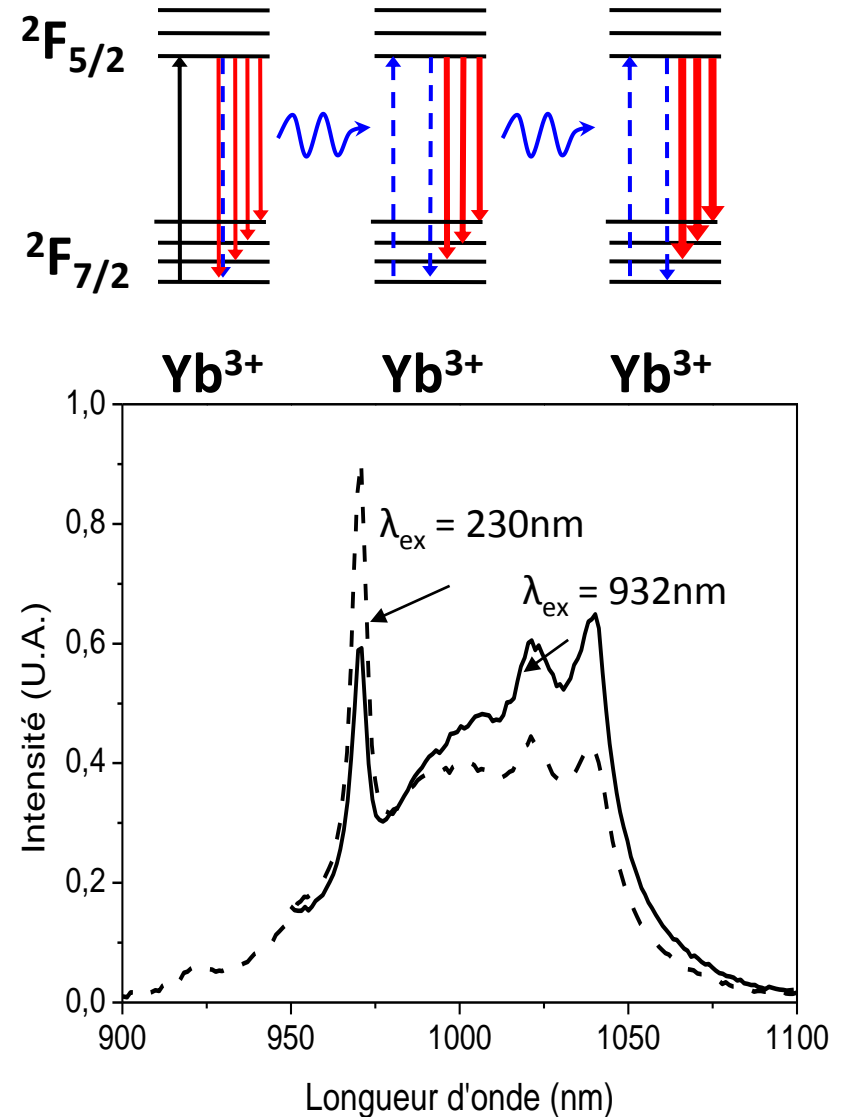


- Excitation plasma: [e⁻ · h⁺]
Augmentation de la taille des cristallites →
Augmentation du volume excité
- Excitation 254 nm : [hv]
Volume constant du composé excité
Limitation due à l'épaisseur des particules (100-150 nm)

Choix des longueurs d'onde d'excitation



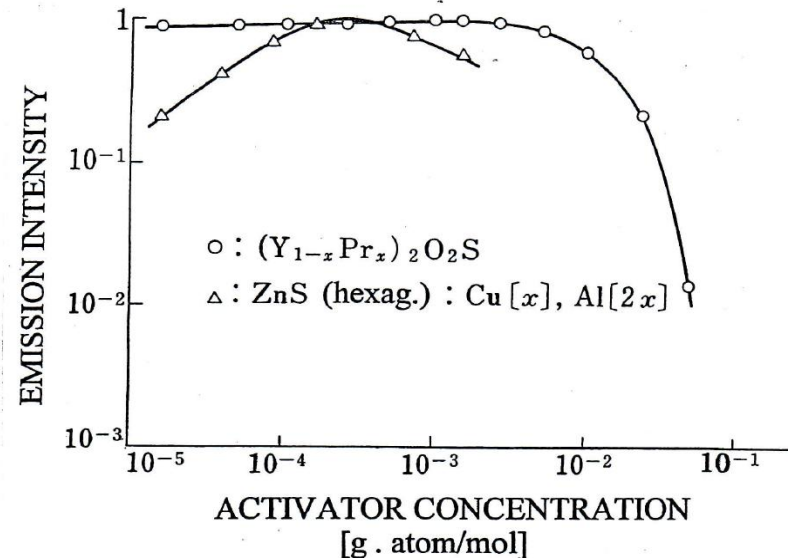
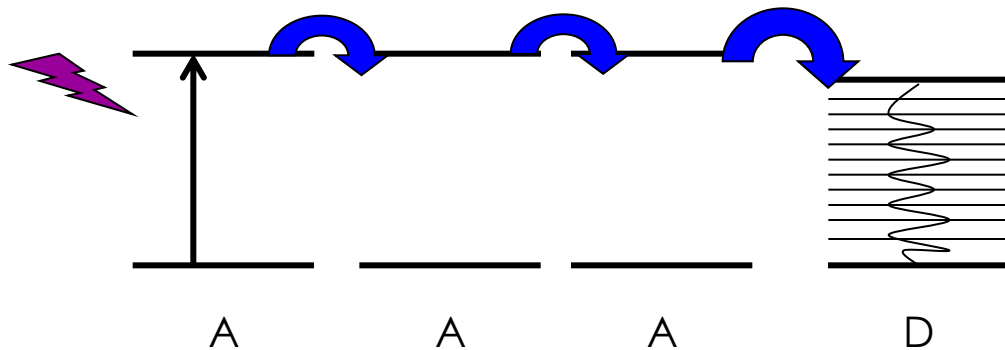
➔ **Déformation importante du spectre aux faibles énergie**



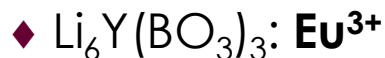
Effet de concentration

Transfert d'énergie entre centres identiques

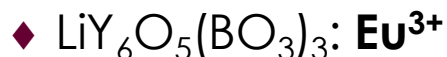
Extinction par concentration



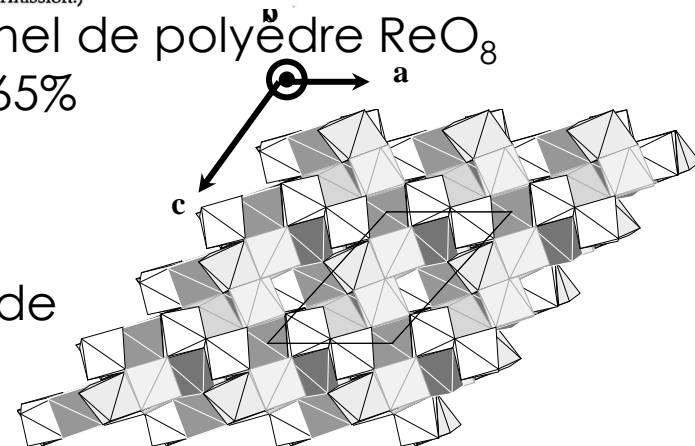
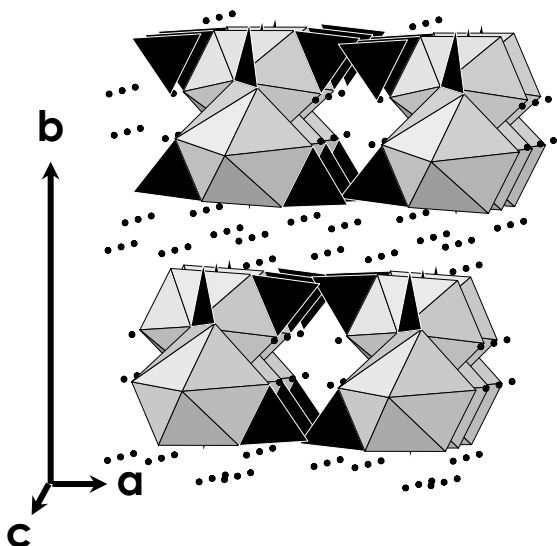
Activator concentration dependence of the cathode-luminescence intensities of $Y_2O_3:Eu^{3+}$ and $ZnS:Cu$. (From Kubonita, S., Kawai, H., and Hoshina, T., *Jpn. J. Appl. Phys.*, 19, 1647, 1980. With permission.)



Réseau Mono-dimensionnel de polyèdre ReO_8
% subs molaire max Eu^{3+} 65%

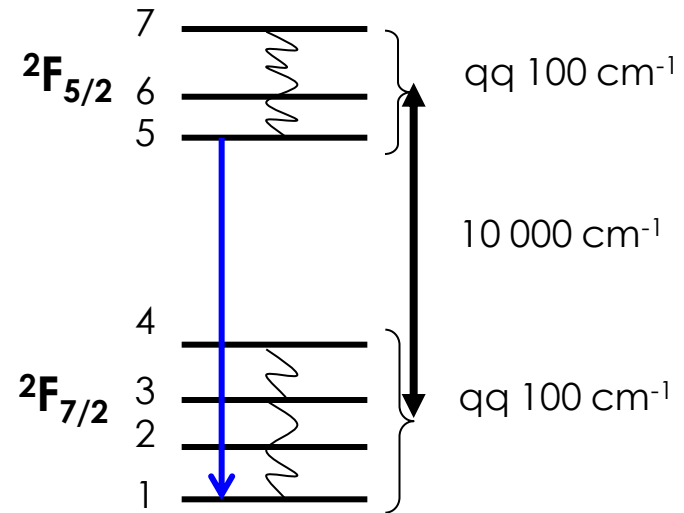
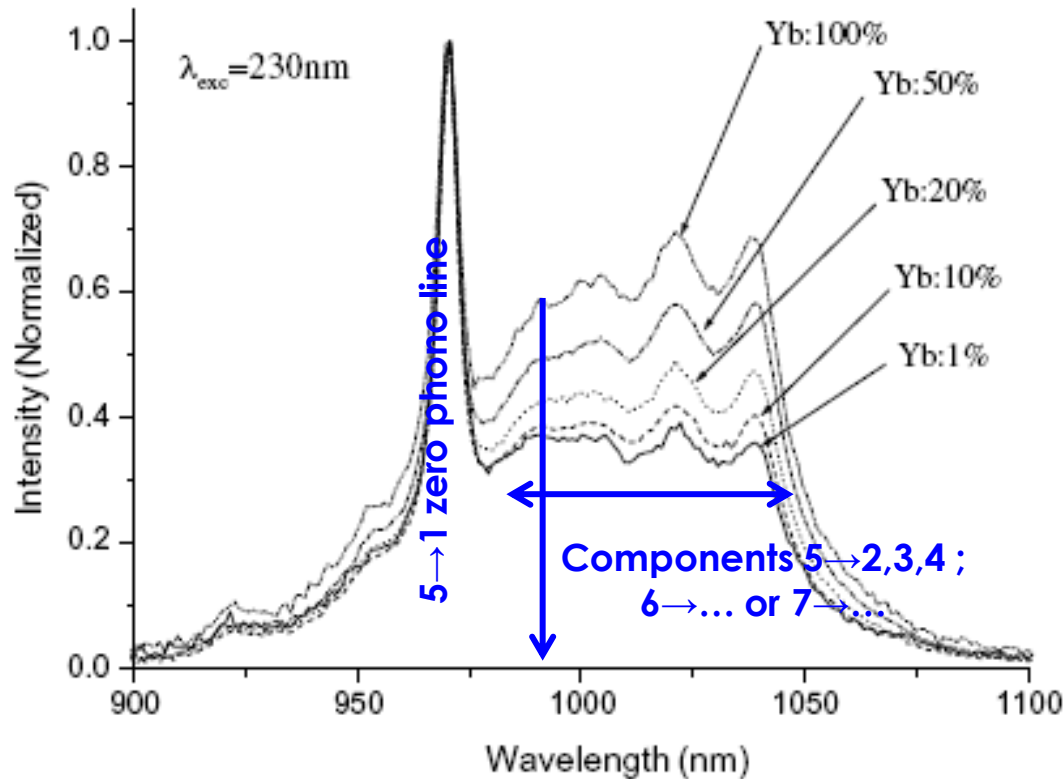


Réseau tri-dimensionnel de polyèdres ReO_8 et ReO_7
% subs molaire max Eu^{3+} 10%



Effet de concentration

Yb^{3+} ion ($4f^{13}$)

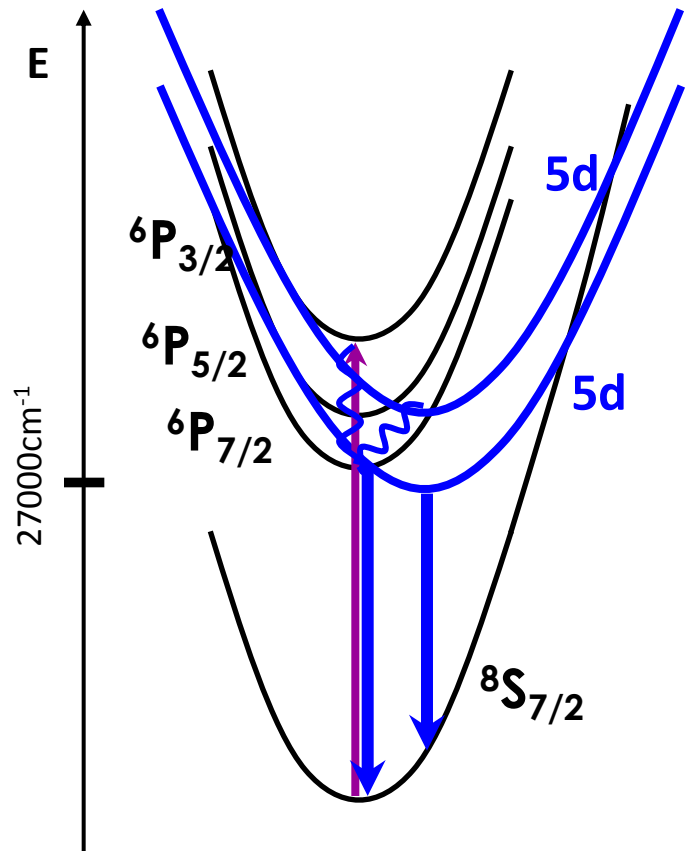


Forte déformation des spectres aux basses énergies

Fig. 3. Normalized emission spectra of the Yb-doped $\text{Li}_6\text{Y}(\text{BO}_3)_3$ for an excitation at 230 nm (% molar substitution rate).

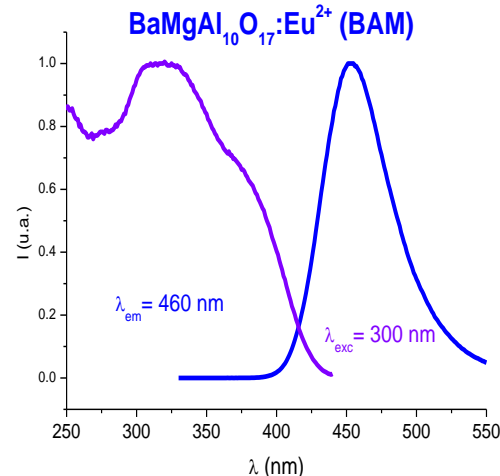
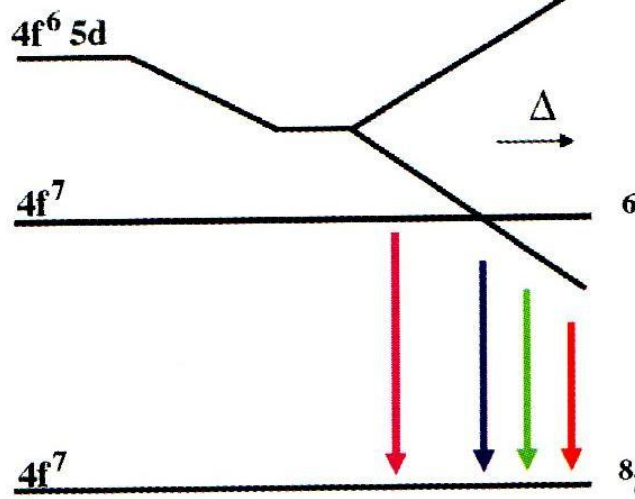
Champ cristallin et localisation des dopants

Eu²⁺ ion (4f⁷)



5d → 8S_{7/2} Transitions
ou
6P_{7/2} → 8S_{7/2}

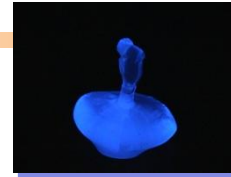
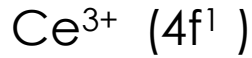
Eclatement des 5d par le champ cristallin



Emission Eu²⁺ au sein de différentes matrices

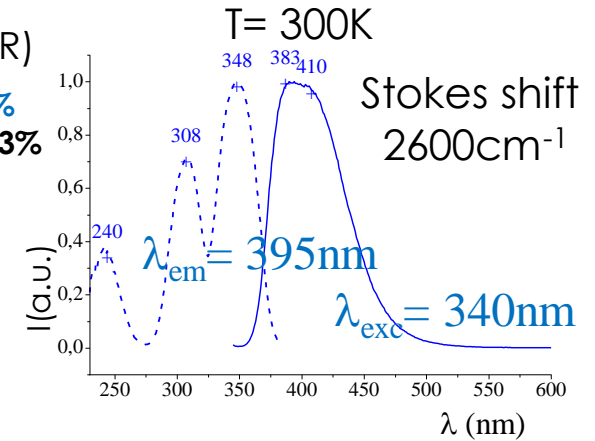
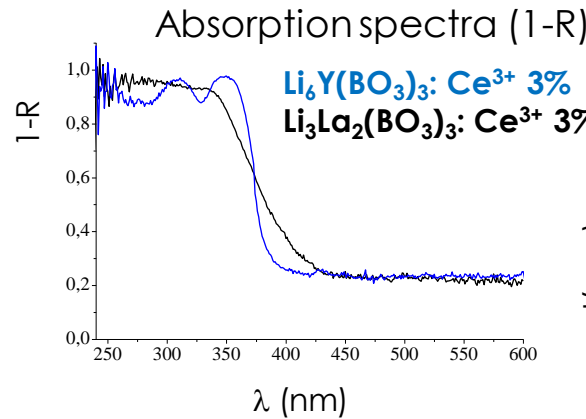
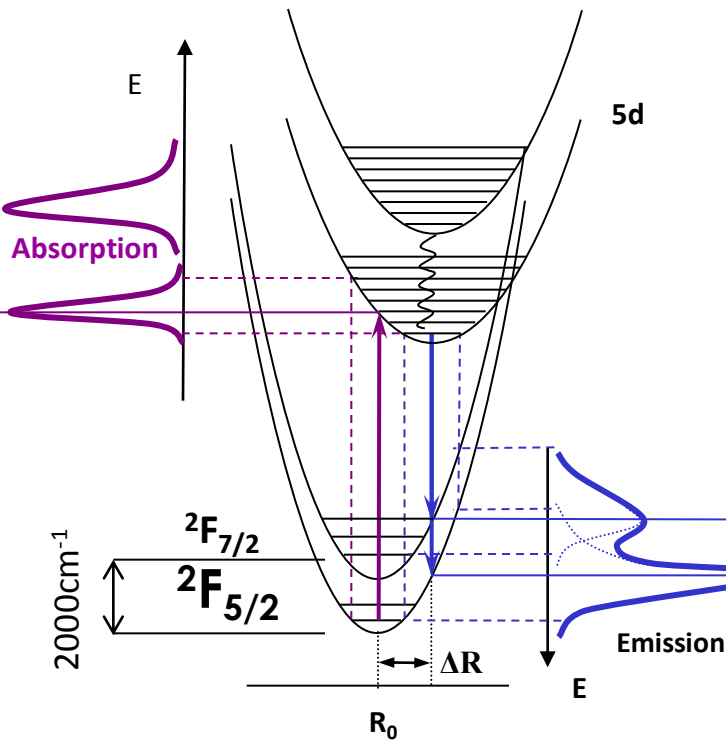
SrB ₄ O ₇ :Eu	368 nm
Sr ₂ P ₂ O ₇ :Eu	420 nm
BaMgAl ₁₀ O ₁₇ :Eu	453 nm
Sr ₄ Al ₁₄ O ₂₅ :Eu	490 nm
Ba ₂ SiO ₄ :Eu	505 nm
SrGa ₂ S ₄ :Eu	535 nm
Sr ₂ SiO ₄ :Eu	575 nm
SrS:Eu	615 nm

Champ cristallin et localisation des dopants

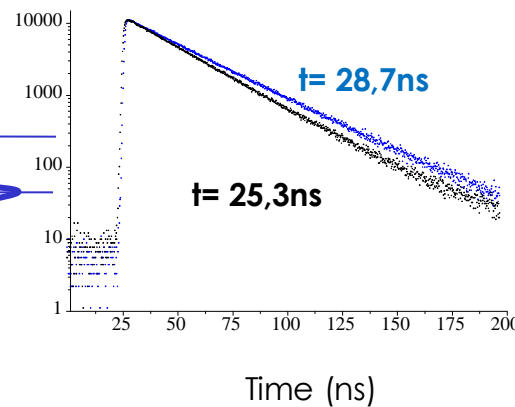


Li₆Y(BO₃)₃: Ce³⁺ 3%

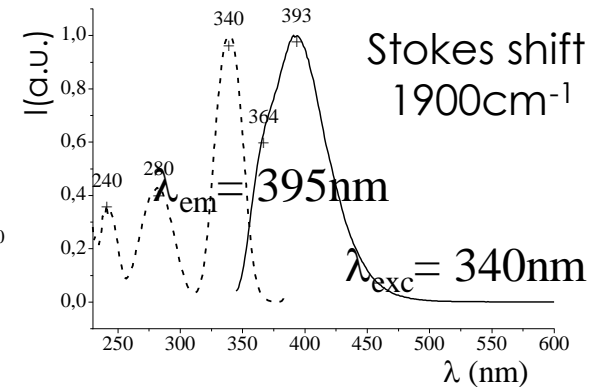
Transitions permises



Decay curves



Li₃La₂(BO₃)₃: Ce³⁺ 3%



GDR Verres- Atelier des terres rares

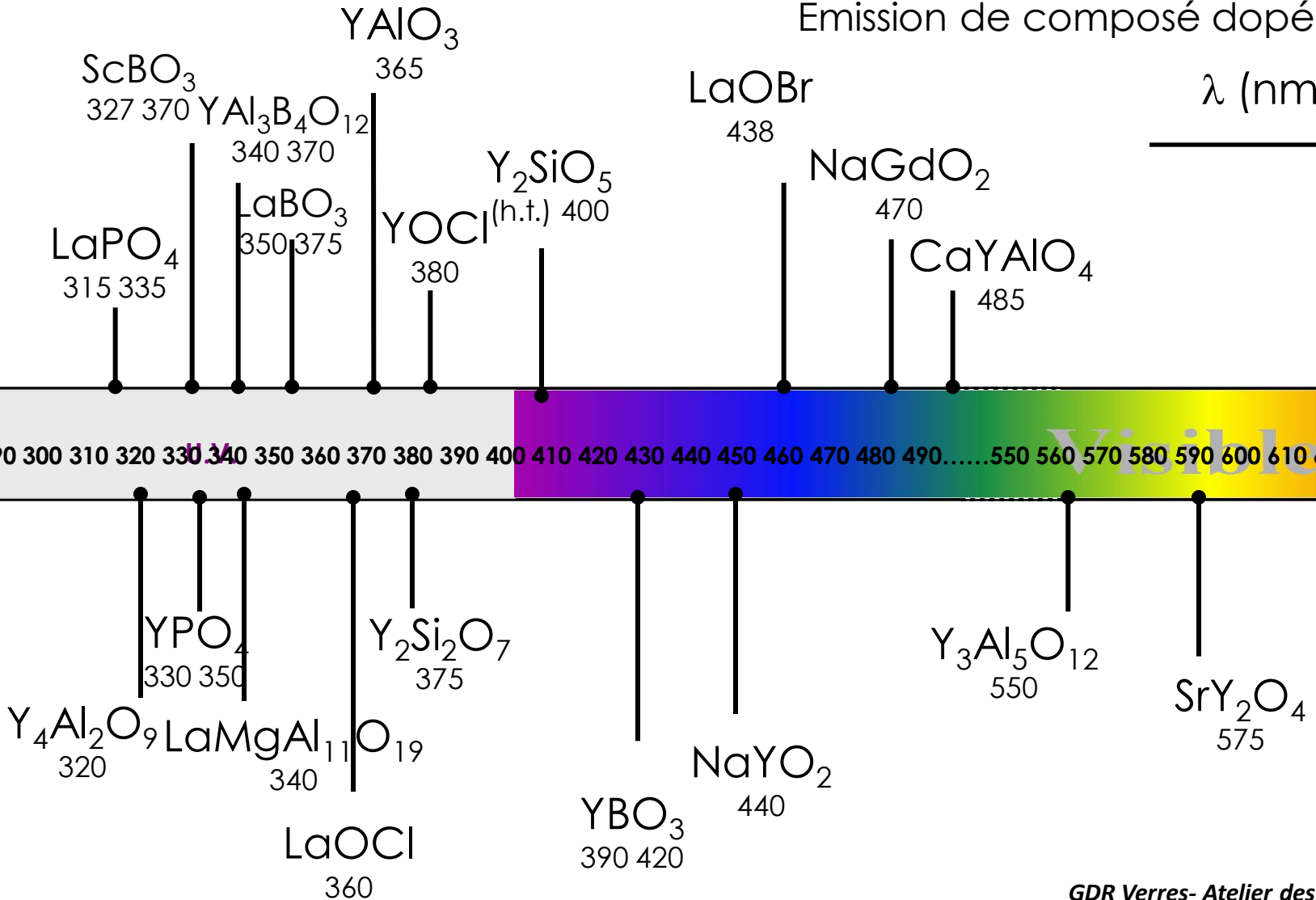
Nice 10-11 Septembre 2012

Champ cristallin et localisation des dopants

Ce³⁺ (4f¹)

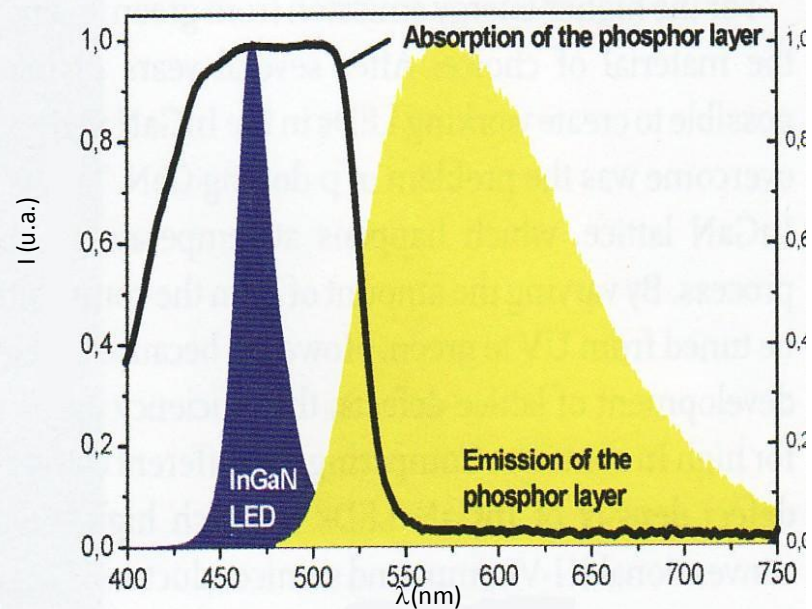
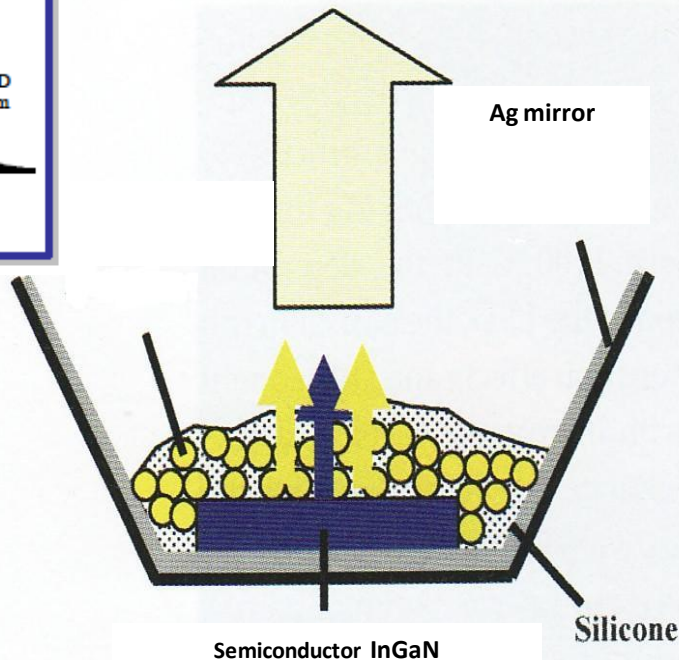
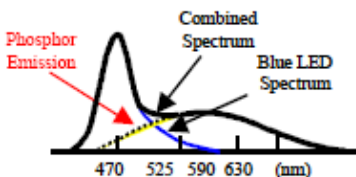
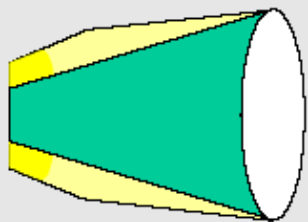
Emission de composé dopé au Ce

λ (nm)



Champ cristallin et localisation des dopants

Génération d'émission blanche pour l'éclairage



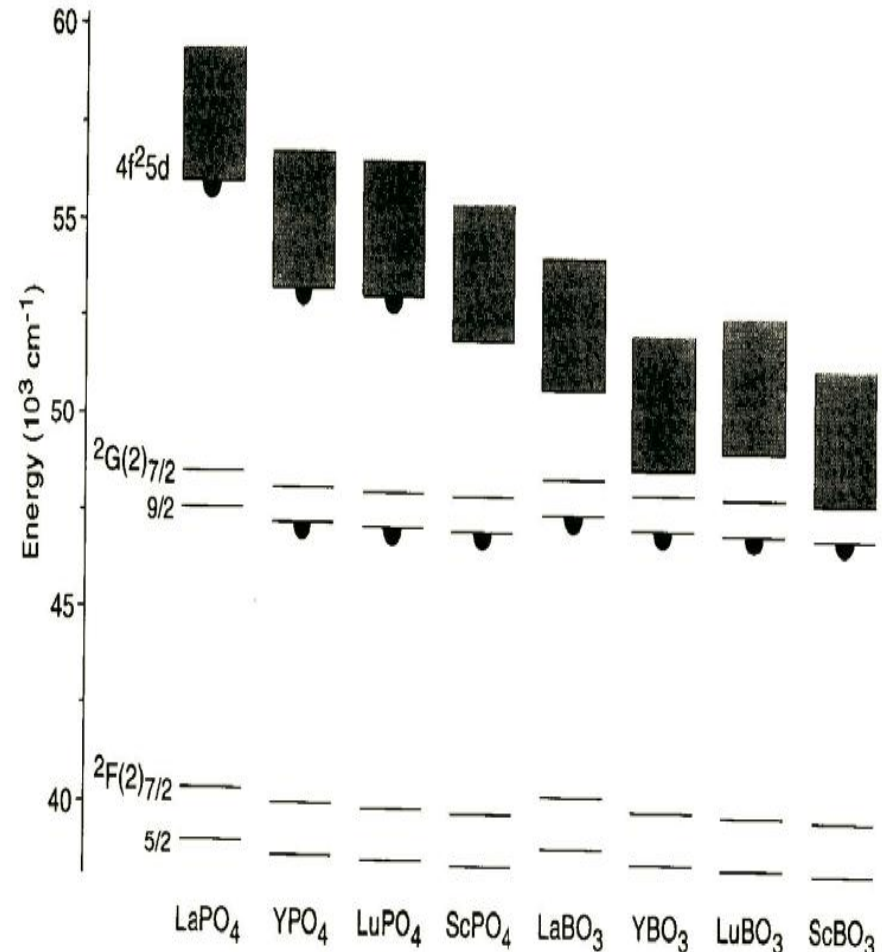
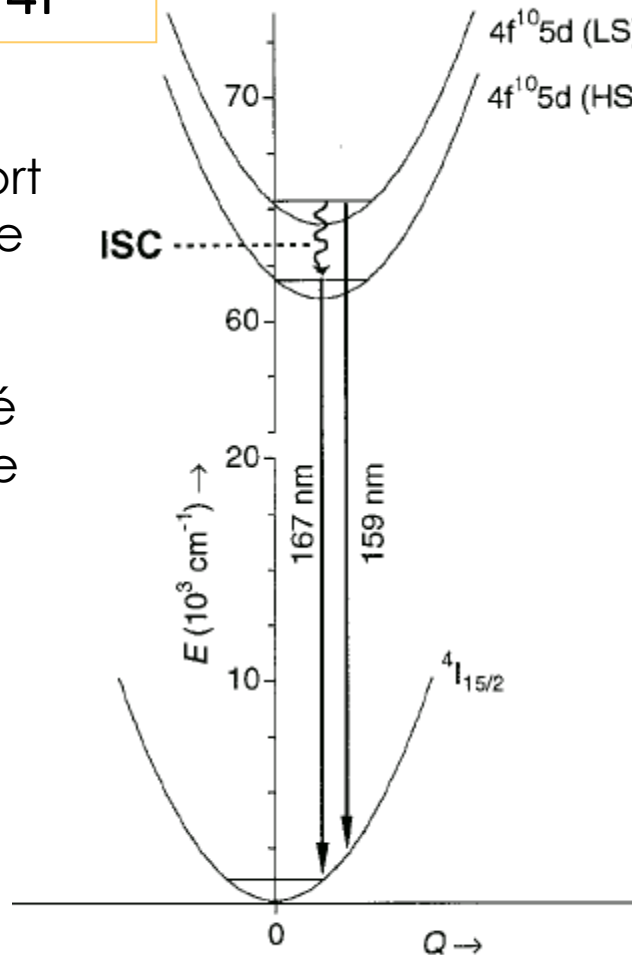
Champ cristallin et localisation des dopants

Critères pour une application en scintillation (imagerie médicale)

Ce³⁺ 4f¹
Nd³⁺ 4f³⁺/Pr³⁺ 4f²

- ◆ Réseau à fort gap/CC faible émission d→f
- ◆ Forte densité
- ◆ Durée de vie courte (ns)

Emissions observées pour des matériaux dopés Nd³⁺

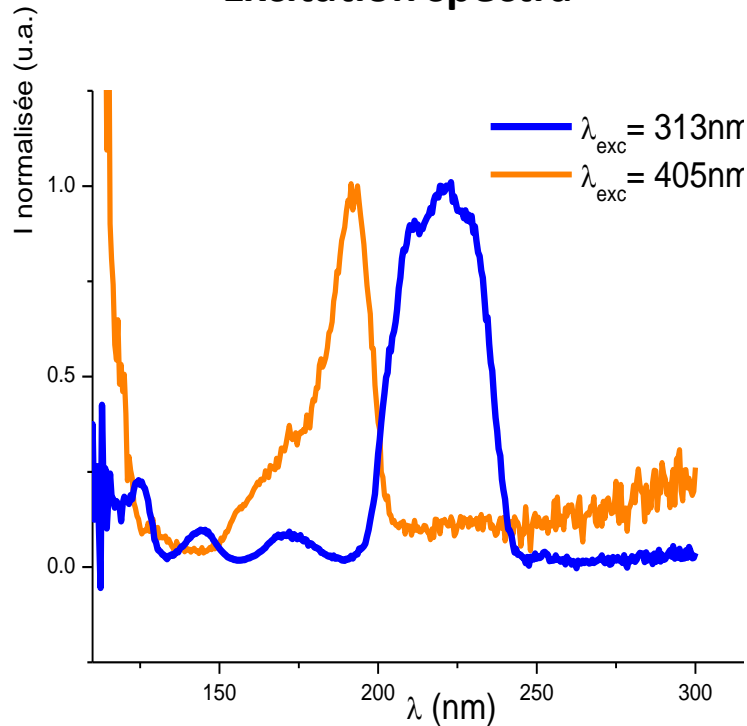


Champ cristallin et localisation des dopants

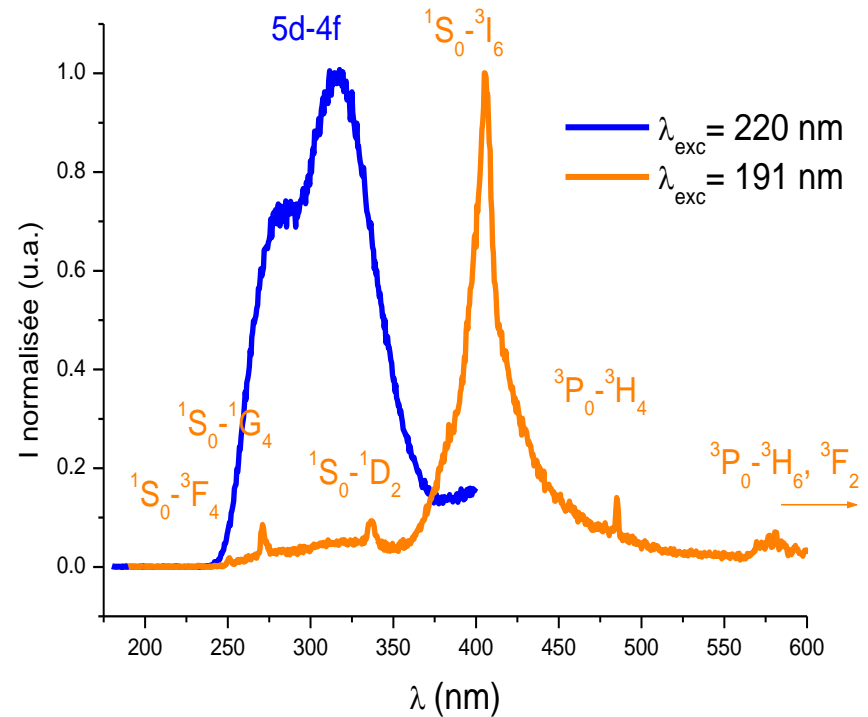
$\text{Pr}^{3+} 4f^2$

Réseaux halogénés

Excitation spectra



Emission spectra

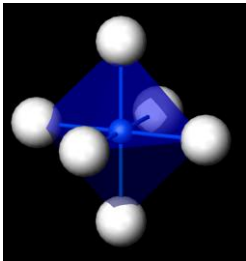
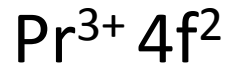


Localisation de la terre rare au sein de 2 polyèdres de coordination

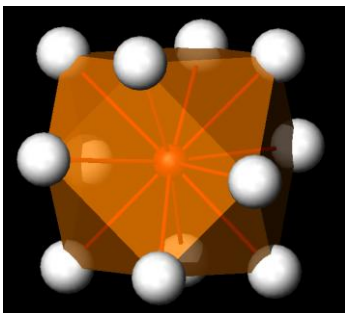
➔ **Site 1:** 5d→4f emission

Site 2: 4f→4f emission

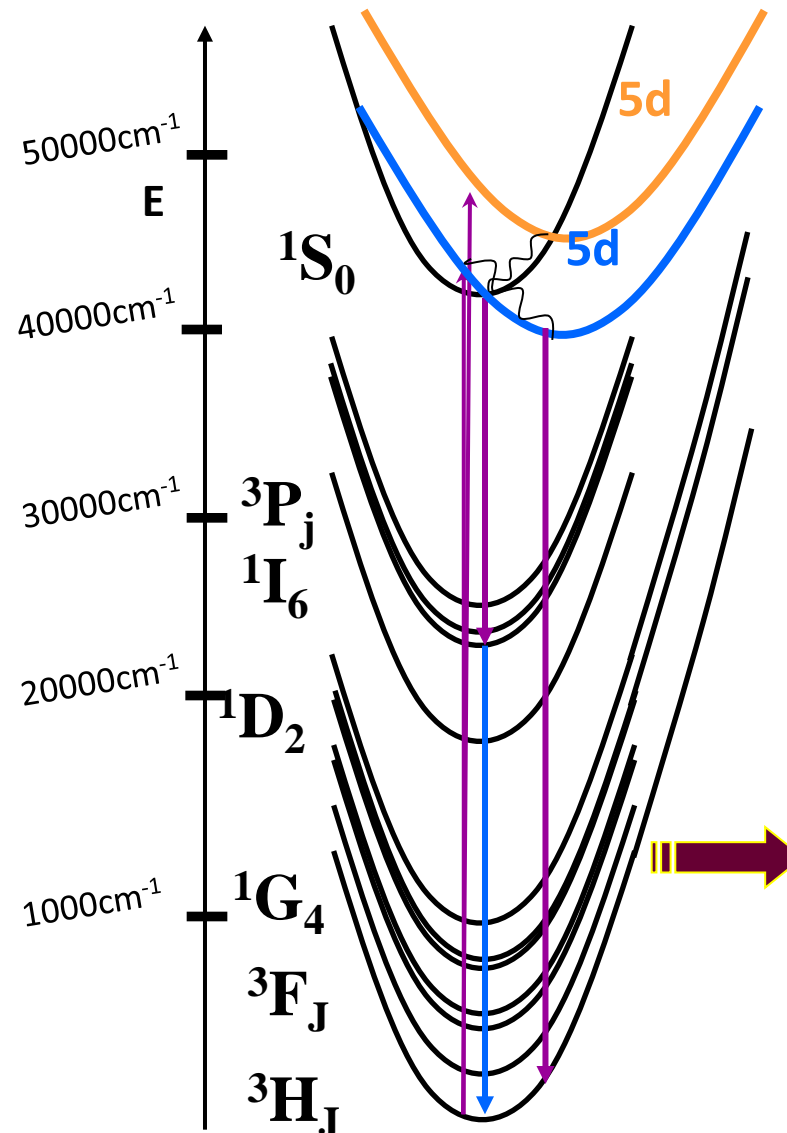
Champ cristallin et localisation des dopants



Site Octaédrique
 $d\text{Ln-X}=2.15\text{A}$



Site [12]
 $d\text{Ln-X}=3.35\text{A}$



Importance du site
de substitution

Champ cristallin et localisation des dopants

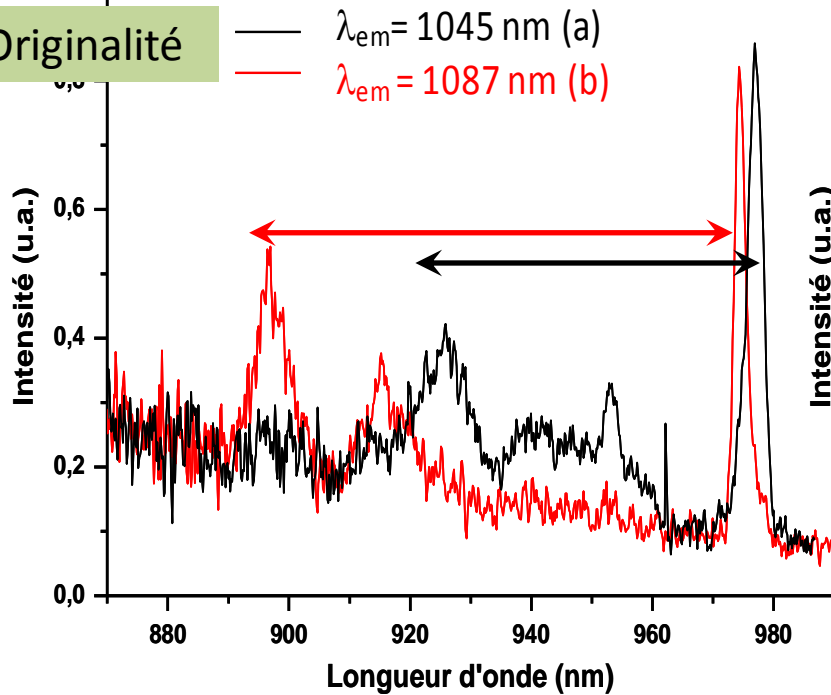
Composé $\text{LiGd}_6\text{O}_5(\text{BO}_3)_3 : \text{Yb}$

4 sites LnO_7
2 sites LnO_8

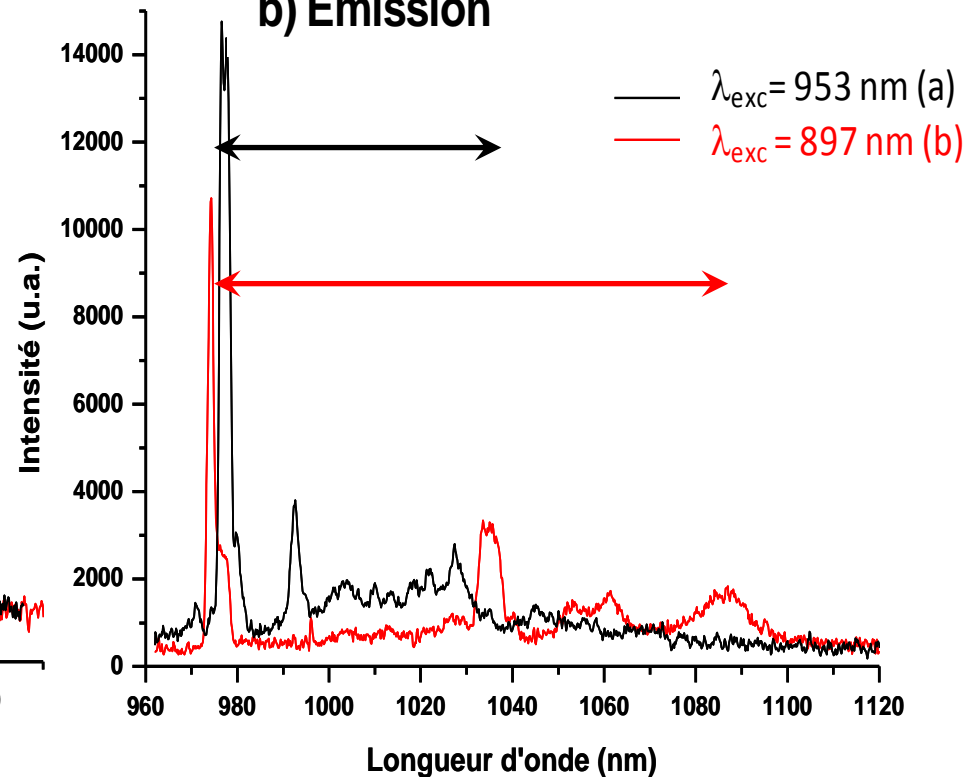
Yb^{3+}

Originalité

a) Excitation



b) Emission



Mise en évidence
de 2 répartitions
spectrales

Eclatement répartition type a

<

Eclatement répartition type b

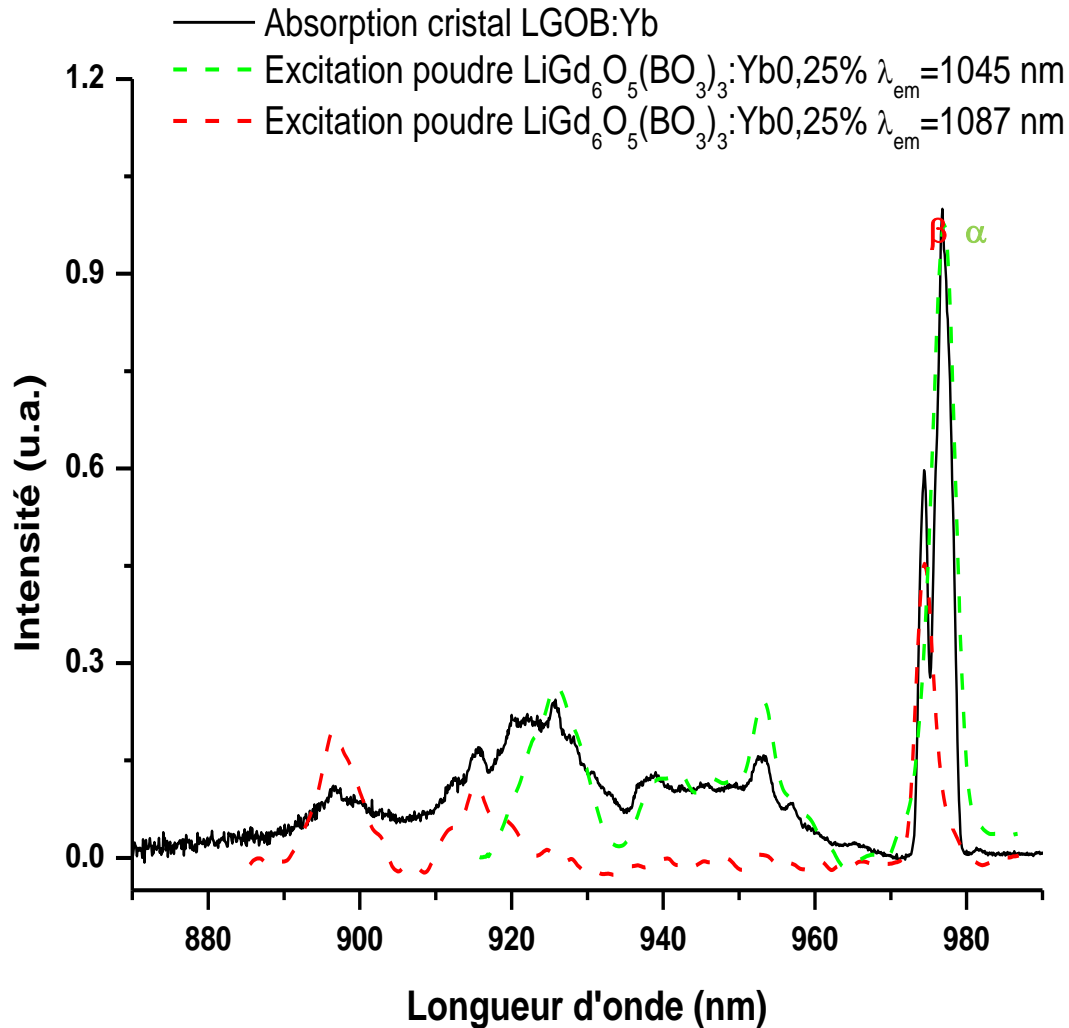
GDR Verres- Atelier des terres rares

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Champ cristallin et localisation des dopants

Yb³⁺

Composé LiGd₆O₅(BO₃)₃ : Yb



Attribution

α - site [7]

β - site [8]

Conclusion

Du matériau cristallisé au verre...

Transposition de l'ensemble des propriétés de PL présentées

Nuance: sonde structurale/dénombrement des sites (élargissement des spectres en environnement désordonnés)

Merci de votre attention