Materials for white-LED: efforts for Ab initio Materials Design

M. Mikami *et al*., IOP Conf. Ser.: Mater. Sci. Eng. 1, 012002 (2009)
M. Mikami, N. Kijima, B.Bertrand, M.Stankovski, X.Gonze, *ibid* (in press).

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*** CERDECAM, Institut Supérieur Industriel ECAM, Belgium**

ABINT 2011 Workshop (11-14 April, 2011, Han-sur-Lesse, Belgium)

MITSUBISHI CHEMICAL GROUP
SCIENCE AND TECHNOLOGY RESEARCH CENTER, INC.

Phosphor-converted white LEDs

Conventional type:

Blue-LED + yellow phosphor

(typically, $Y_3Al_5O_{12}:Ce^{3+}$)

New (Next) type:

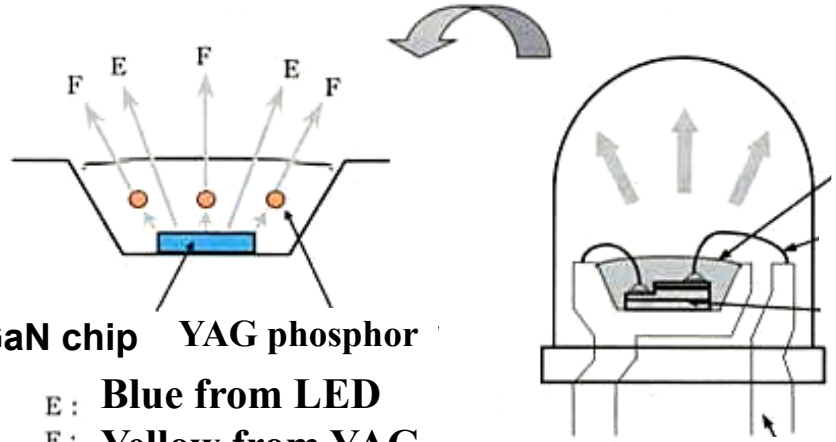
High color rendering types

Blue-LED + yellow & red

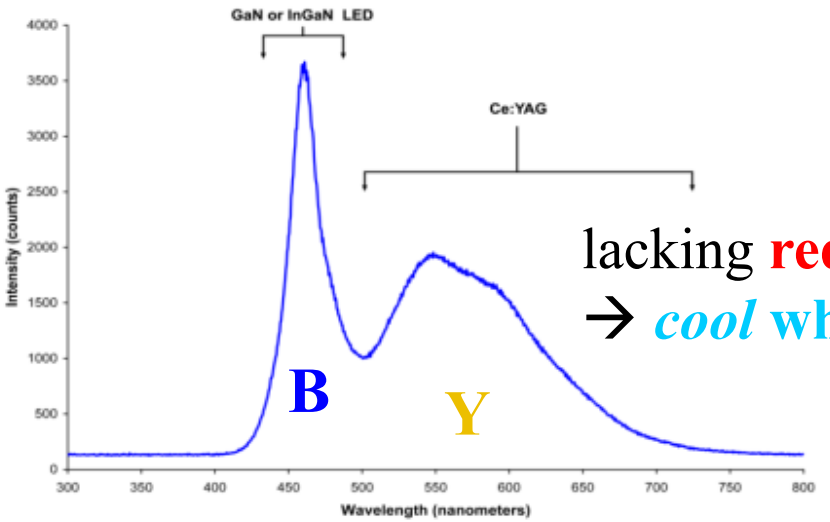
Near UV-LED + blue & green & red

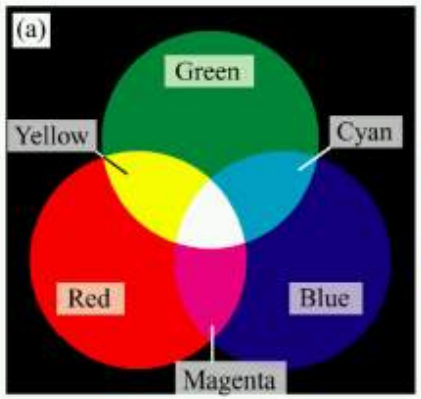
Blue-LED + green & red

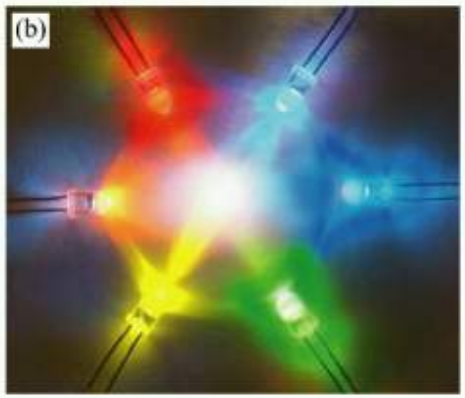
***New phosphors* to be explored !**



YAG : Yttrium Aluminum Garnet $(Y_a,Gd_{1-a})_3(Al_b,Ga_{1-b})_5O_{12} : Ce^{3+}$







"www.lightemittingdiodes.org"

WE NEED *GUIDING PRINCIPLES (THEORY)* !

"Phosphor Handbook" (2006) + **updates (from literatures)**

Business through Innovation

Phosphor	Emission color	Crystal structure	References
Y-Si-O-N:Ce^{3+}	Blue	—	[3]
$BaAl_{11}O_{16}N:Eu^{2+}$	Blue	β-Alumina	[2,4]
JEM:Ce^{3+}	Blue	Orthorhombic	[19]
$SrSiAl_2O_3N_2:Eu^{2+}$	Blue-green	Orthorhombic	[14]
$SrSi_5AlO_2N_7:Eu^{2+}$	Blue-green	Orthorhombic	[14]
$BaSi_2O_2N_2:Eu^{2+}$	Blue-green	Monoclinic	[18]
α-SiAlON:Yb^{2+}	Green	Hexagonal	[15]
β-SiAlON:Eu^{2+}	Green	Hexagonal	[17]
$MYSi_4N_7:Eu^{2+}$ (M = Sr, Ba)	Green	Hexagonal	[12]
$MSi_2O_2N_2:Eu^{2+}$ (M = Ca, Sr)	Green-yellow	Monoclinic	[18]
α-SiAlON:Eu^{2+}	Yellow-orange	Hexagonal	[7,8,10,11]
$LaSi_3N_5:Eu^{2+}$	Red	Orthorhombic	[6]
$LaEuSi_2N_3O_2$	Red	Orthorhombic	[6]
$Ca_2Si_5N_8:Eu^{2+}$	Red	Monoclinic	[5]
$M_2Si_5N_8:Eu^{2+}$ (M = Sr, Ba)	Red	Orthorhombic	[5]
$CaAlSiN_3:Eu^{2+}$	Red	Orthorhombic	[20]

blue(-green) nitride?!

AlN:Eu2+,Si4+

$BaSi_7N_{10}$:Eu2+

$Ba_3Si_6O_{12}N_2$:Eu2+

$Ba_3Si_6O_9N_4$:Eu2+

$Ba_1Si_2O_2N_2$:Eu2+

$Sr_1Si_2O_2N_2$:Eu2+

$Ca_1Si_2O_2N_2$:Eu2+

-SiAlON:Eu2+

$LaSi_3N_5$:Ce3+

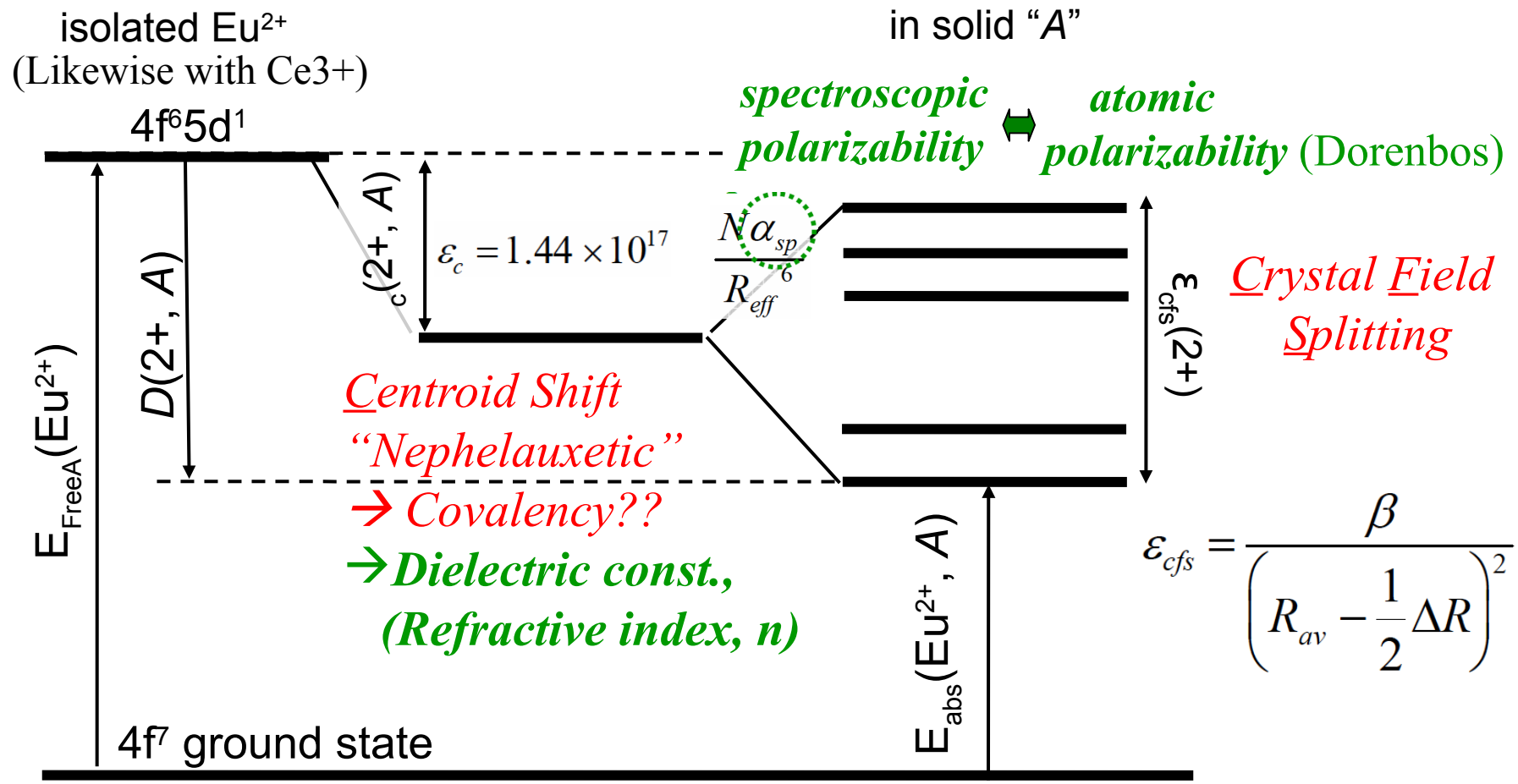
$La_3Si_6N_{11}$:Ce3+

(Sr,Ca)$AlSiN_3$:Eu2+

$SrAlSi_4N_7$:Eu2+

From oxides to (oxy)nitrides (or sulfides)

MM



Eu²⁺/Ce³⁺ in "more covalent host" exhibits longer τ_{em} ? ... Not always!

Notations based on Dorenbos

More polarizable (More "MO"), longer λ_{em}

MM

Business through Innovation

from MM & Kijima, Opt. Mater. (2010)

covalent "$2SrO+SiO_2$" "$3SrO+SiO_2$" "SrO" *ionic*

Sr_2SiO_4:Eu

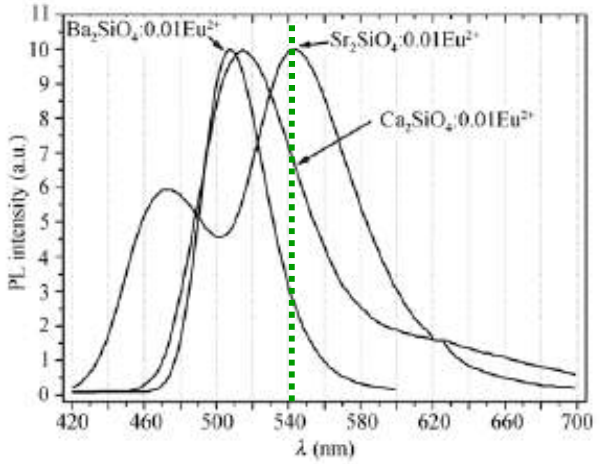


Figure 2 Emission spectra of $Ca_2SiO_4:Eu^{2+}$, $Sr_2SiO_4:Eu^{2+}$ and $Ba_2SiO_4:Eu^{2+}$ (λ_{ex} = 370 nm)[24].

Sr_2SiO_4: 3.16, 3.28, 3.18

XiXian, Chin. Sci. Bull.(2008)

Sr_3SiO_5:Eu

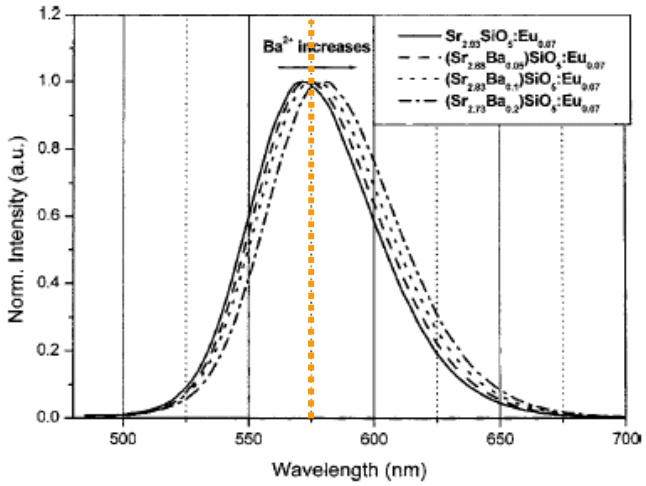


FIG. 1. Emission spectra of $Sr_{2.93}SiO_5:Eu_{0.07}$ phosphor as a function of Ba^{2+} concentration.

Sr_3SiO_5: 3.33, 3.33, 3.35

Park, Appl.Phys.Lett.(2006)

SrO:Eu

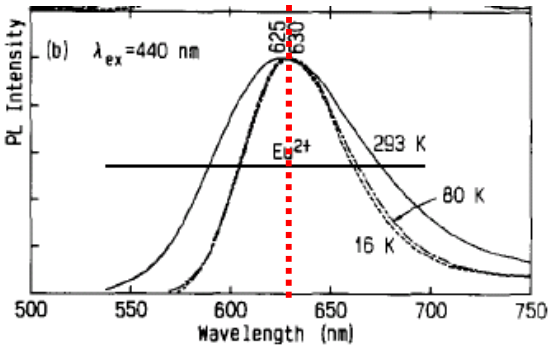


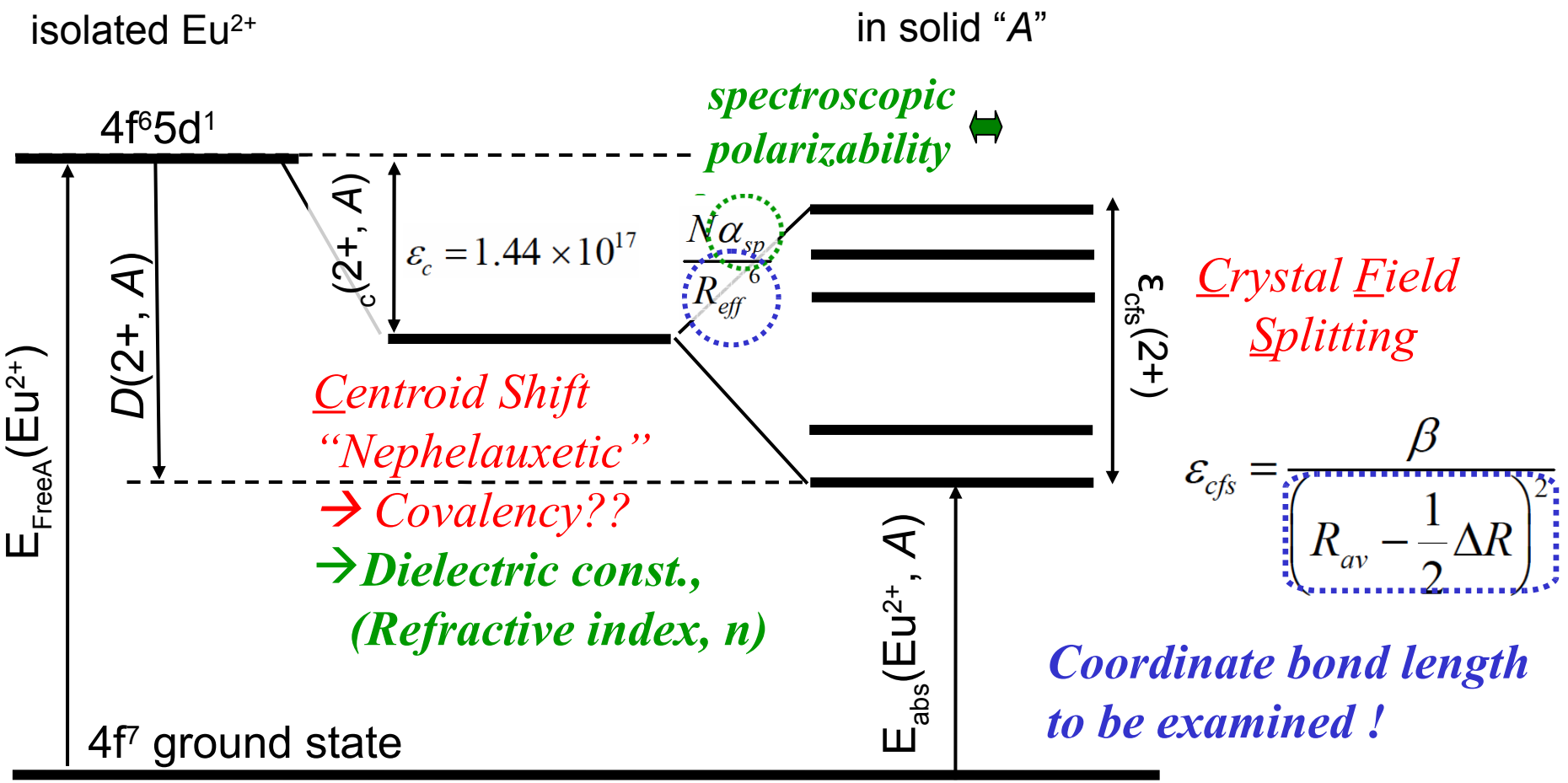
Fig. 3. Photoluminescence (PL) spectra of the SrO:EuF_3 (0.5 mol%) powder phosphor which was prepared in an atmosphere of H_2. The PL spectra were obtained under excitation (a) at 280 nm in the charge transfer (CT) band (see Fig. 2) and (b) at 440 nm in the T_{2g} band (see Fig. 4).

SrO: 3.76, 3.76, 3.76

Yamashita, J.Lumin (1994)

dielectric const.($_{xx}$ $_{yy}$ $_{zz}$*) by ABINIT (Density functional Perturbation Theory)*

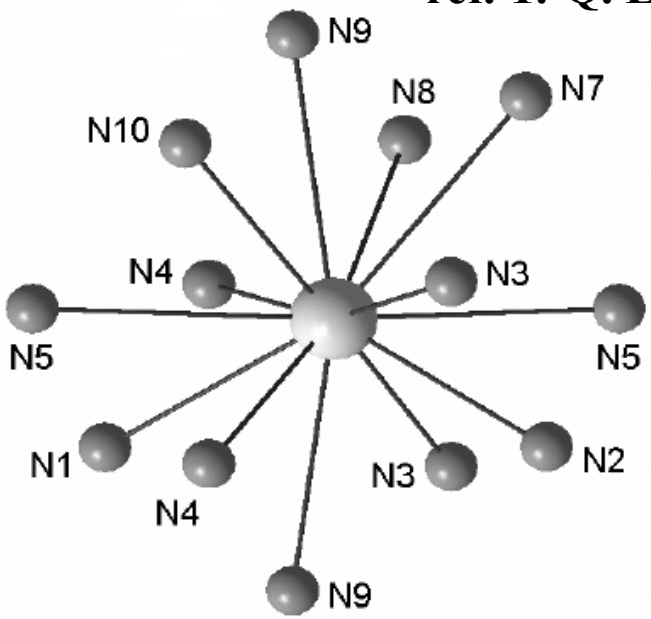
From oxides to (oxy)nitrides (or sulfides)



Notations based on Dorenbos

$BaSi_7N_{10}$:Eu (H.A. Höppe's Thesis - 2003)

ref. Y.-Q. Li *et al.* (2009)



Ba1: 1

$Ba[Si_7N_{10}]:Eu^{2+}$ (CN = 13) **v.s.**

$Ba_2[Si_5N_8]:Eu^{2+}$ (CN = 10 bzw. 8+2)

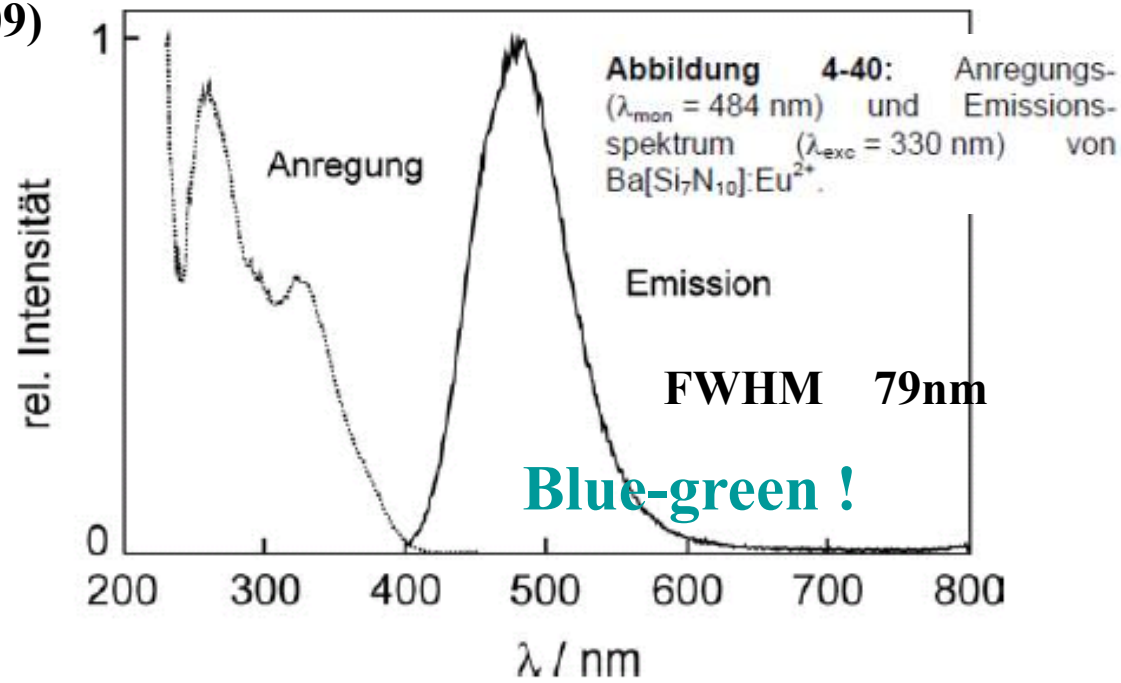


Abbildung 4-40: Anregungs- (λ_{mon} = 484 nm) und Emissions-spektrum (λ_{exc} = 330 nm) von $Ba[Si_7N_{10}]:Eu^{2+}$.

FWHM 79nm

Blue-green !

Tabelle 4-14: Ausgewählte interatomare Abstände / pm in $Ba[Si_7N_{10}]$ gemäß Lit. [129]; die hochgestellten Zahlen in eckigen Klammern geben die Zahl der direkt an die N–Atome gebundenen Si–Tetraederzentren an

Ba(1)	- $N(3)^{[2]}$	291.3(3)	Ba(1)	- $N(9)^{[3]}$	332.3(2)
	- $N(4)^{[2]}$	295.0(4)		- $N(5)^{[3]}$	334.9(3)
	- $N(2)^{[3]}$	307.4(3)		- $N(8)^{[3]}$	340.6(2)
	- $N(1)^{[3]}$	321.3(3)		- $N(7)^{[3]}$	345.0(2)
	- $N(3)^{[2]}$	324.3(3)		- $N(9)^{[3]}$	347.3(2)
	- $N(4)^{[2]}$	324.9(4)		- $N(5)^{[3]}$	352.9(3)
	- $N(10)^{[3]}$	332.3(2)	Ba(1)	- Ba(1)	499.7(1)

c.f. AlN:Eu, Si → Eu site (CN = 12)
by Takeda *et al.*@NIMS, J. Mater. Chem. (2010) 20, 9948

Phosphor $Ba_3Si_6O_{12}N_2:Eu^{2+}$

New green phosphor $Ba_3Si_6O_{12}N_2:Eu^{2+}$

MM

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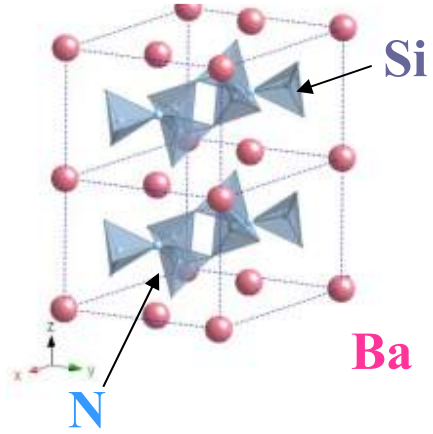
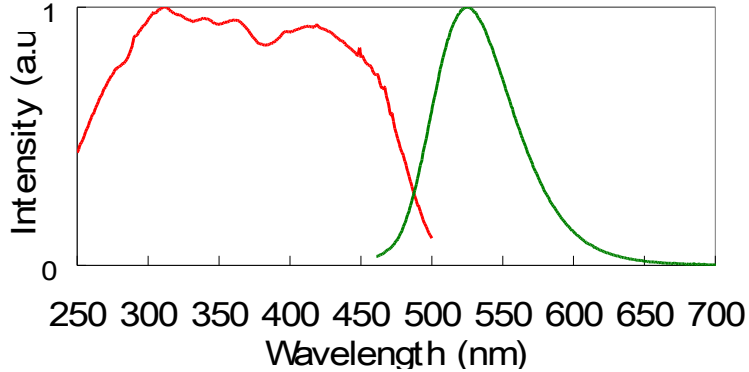
New crystal phase

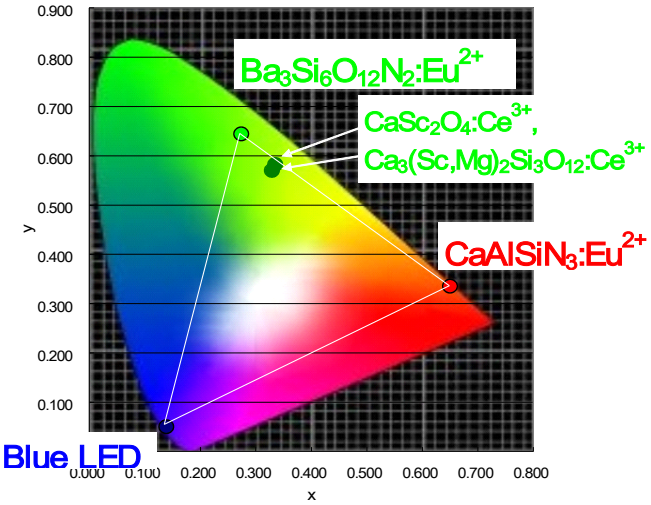


Green luminescence

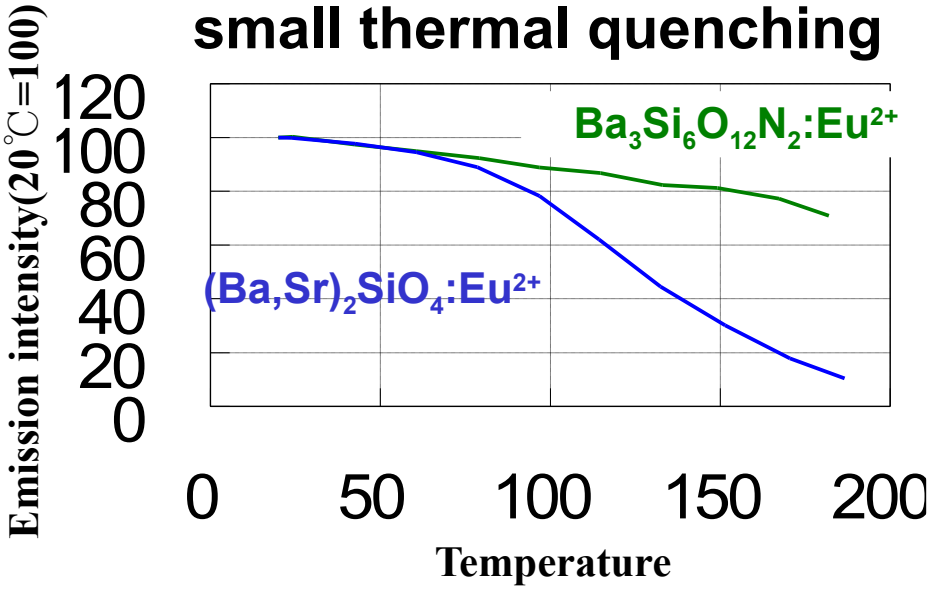
excited by 400-460nm LED light



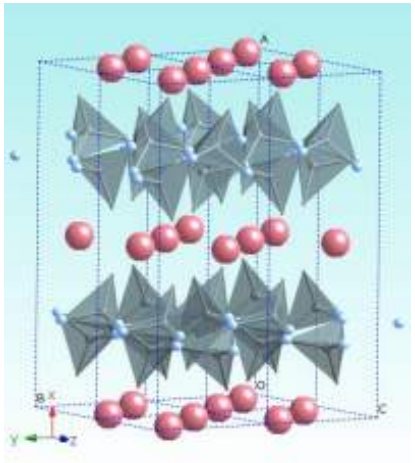
excellent color reproduction



small thermal quenching



(Schnick, Hintzen)
$BaSi_2O_2N_2$ ($Ba_3Si_6O_6N_6$)

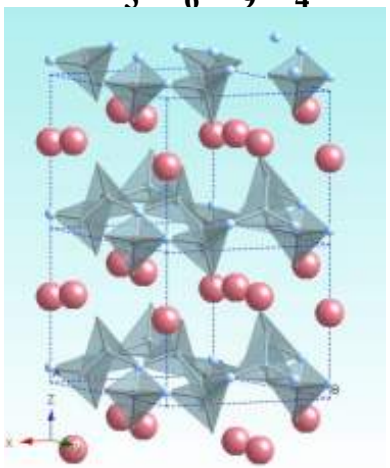


12 anions/(Ba_3+Si_6)

***n*=1.90-1.95**

(Schnick)

$Ba_3Si_6O_9N_4$

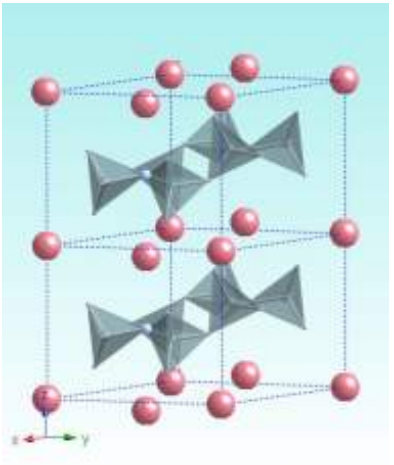


13 anions

***n*=1.81**

(Mitsubishi Chemical)

$Ba_3Si_6O_{12}N_2$

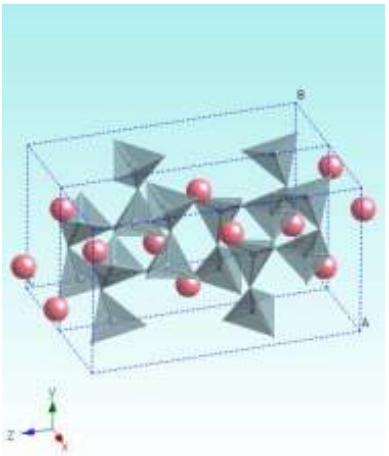


14 anions

***n*=1.76**

("Sanbornite")

$BaSi_2O_5$ ($Ba_3Si_6O_{15}$)



15 anions

***n*=1.65**

N-rich
→larger refractive index *n* ?
(→ calculation)

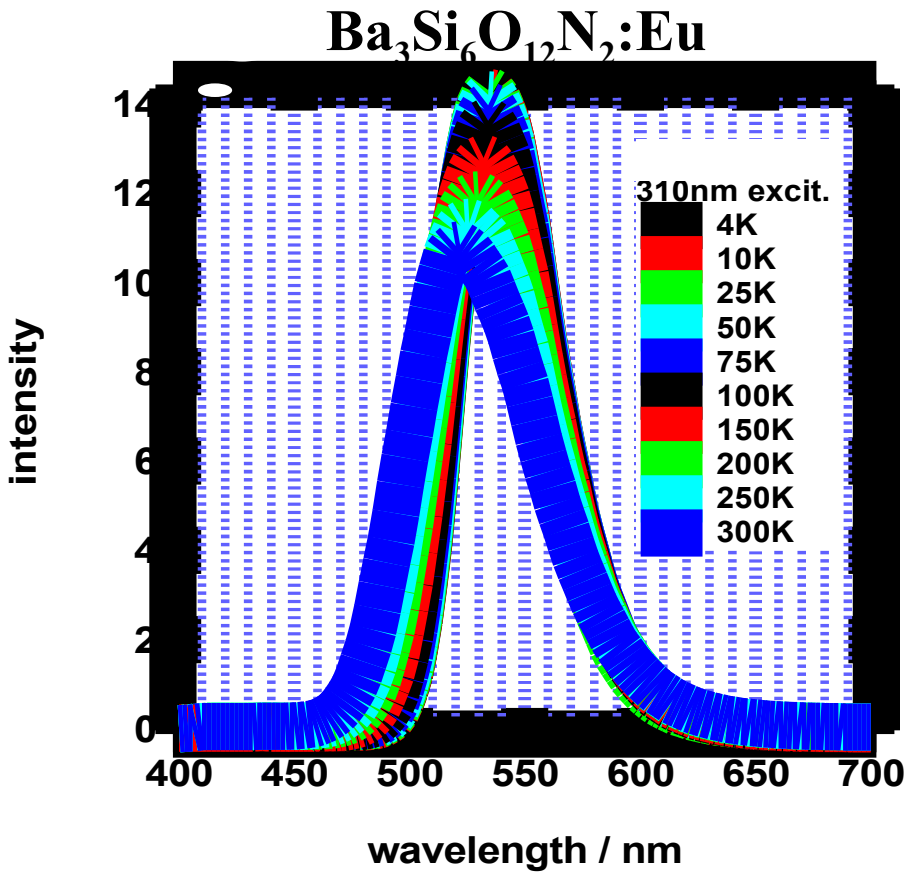
Question:
N-rich
⇒ more polarizable
⇒ longer $_{em}$?

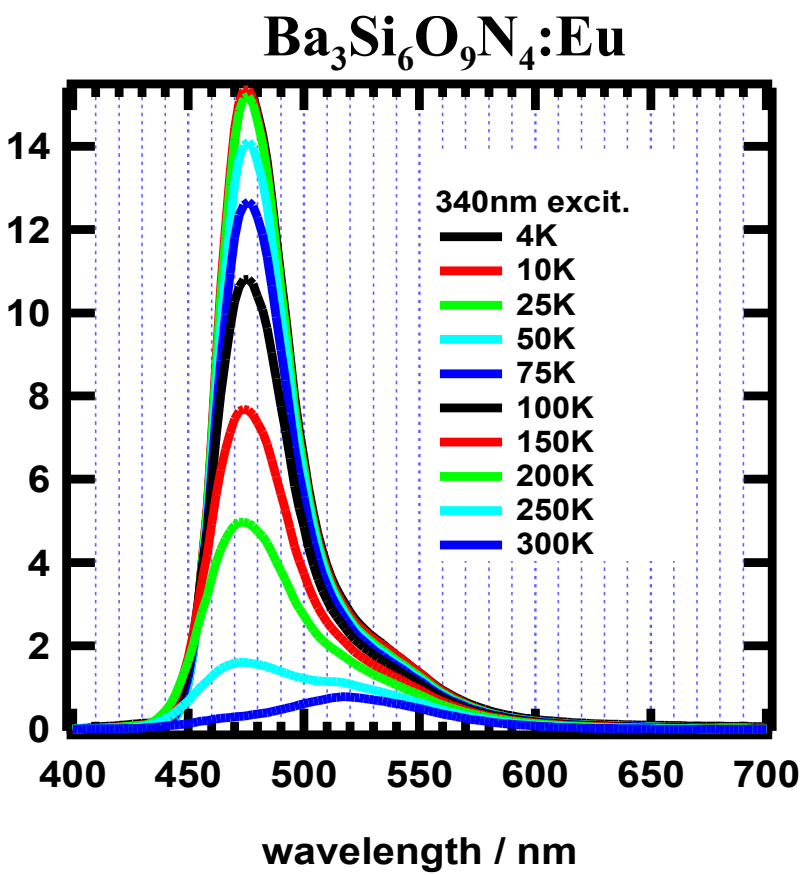
Phosphor $Ba_3Si_6O_{12}N_2:Eu^{2+}$

$Ba_3Si_6O_{12}N_2$ / $Ba_3Si_6O_9N_4$ Eu f-d emission

MM

Business through Innovation





PL peak 530nm (Green)
strong luminescence@R.T.

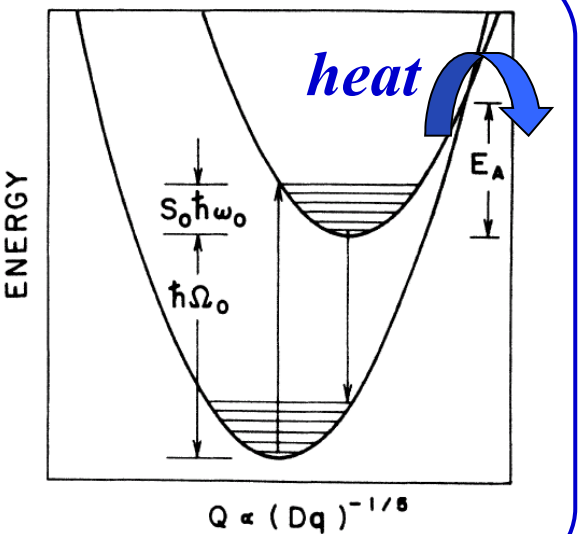
PL peak 480nm (Blue-green)
quenching @ R.T.

Uheda *et al.* (2007), MM *et al.* (2009); see also, C. Braun *et al.*(2010)

Thermal quenching mechanism

Difficult to explain thermal quenching with configurational coordinate diagram…

Natural to explain with *auto-ionization* mechanism



configurational coordinate

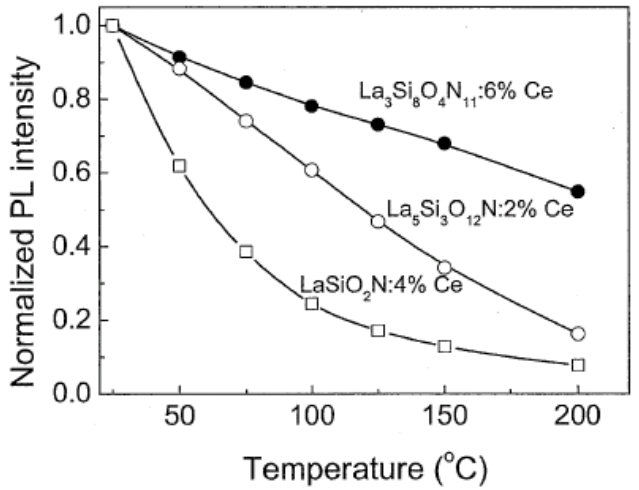


FIG. 10. Temperature-dependent emission intensity of Ce^{3+}-doped lanthanide silicon oxynitrides.

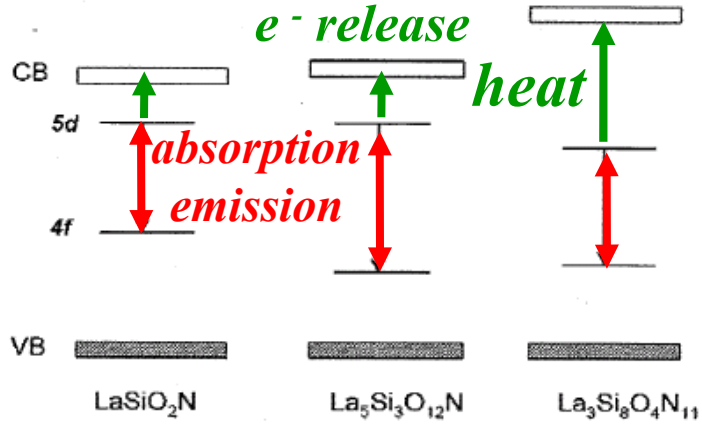
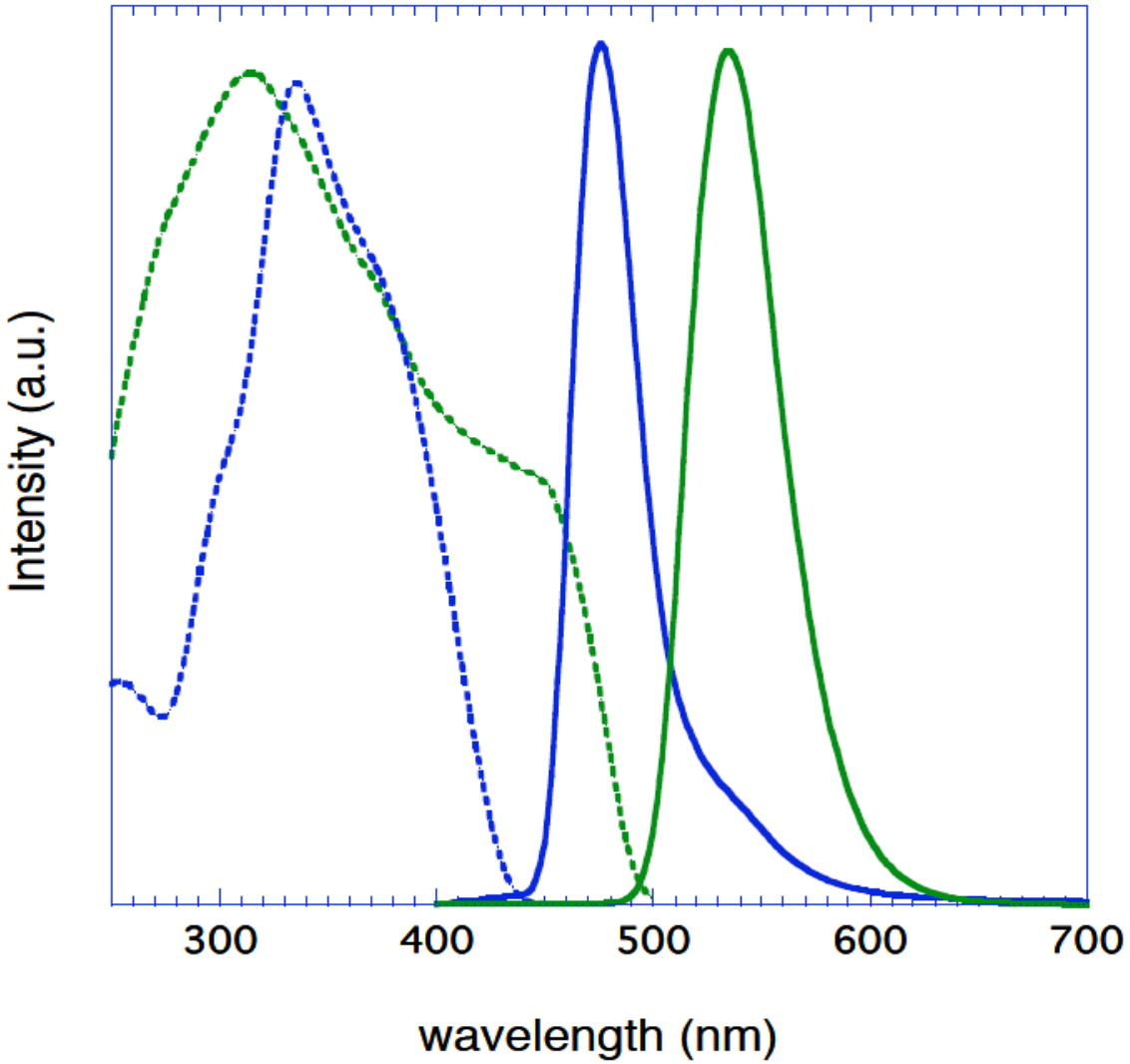


FIG. 12. Schematic illustration of level energies in Ce^{3+}-doped lanthanide silicon oxynitrides [conduction band (CB), valence band (VB)].

B.Dierre *et al.* (2007)

auto-ionization

PL/PLE of $Ba_3Si_6O_{12}N_2$ & $Ba_3Si_6O_9N_4$



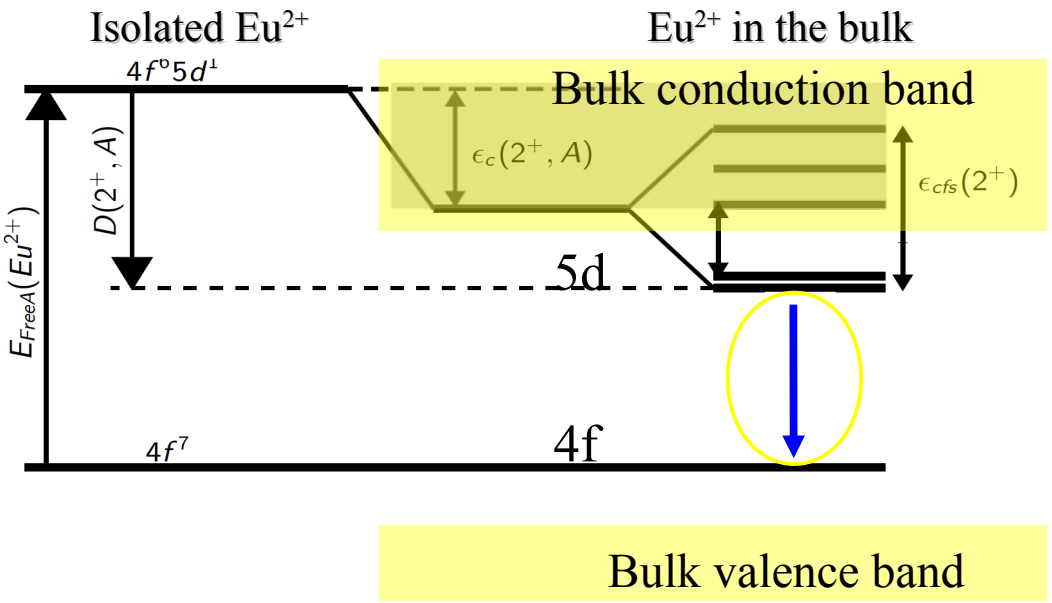
Stokes shift (cm^{-1})

$Ba_3Si_6O_{12}N_2:Eu$ 2790

$Ba_3Si_6O_9N_4:Eu$ 3230

- **Difficult to explain thermal quenching with configurational coordinate diagram…**
- **Natural to explain with *auto-ionization* mechanism**

How to determine the luminescence mechanism from DFT ?

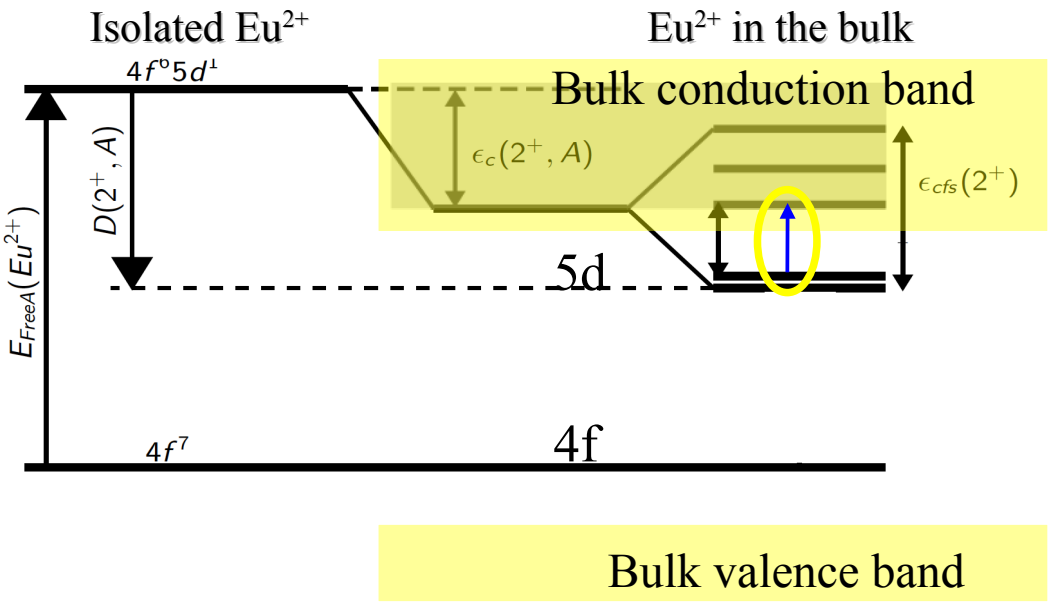


1) Model for photo-emission

Energy gap between the lowest 5d and 4f states of Europium impurities within the host gap

An empirical model

How to determine the luminescence mechanism from DFT ?



1) Model for photo-emission

Energy gap between the lowest 5d and 4f states of Europium impurities within the host gap

2) Model for thermal quenching

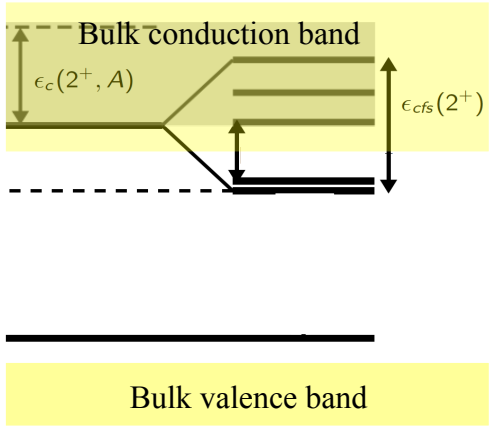
- Auto-ionization of $Eu^{2+} \rightarrow Eu^{3+} + e^-$
- Energy gap between 5d levels of Eu and the conduction band.

P. Dorenbos J.Phys.Cond.Mat.17 (2005)

Calculation for the host $Ba_3Si_6O_{12}N_2$

abinit.org

Crystalline structure of host material ⟹ Electronic structure of host material



Calculation for $Ba_3Si_6O_{12}N_2 : Eu^{2+}$

Position of the 4f and 5d orbitals of Europium ⟺ Position and concentration of Eu impurities ⟺ PAW atomic data for Europium

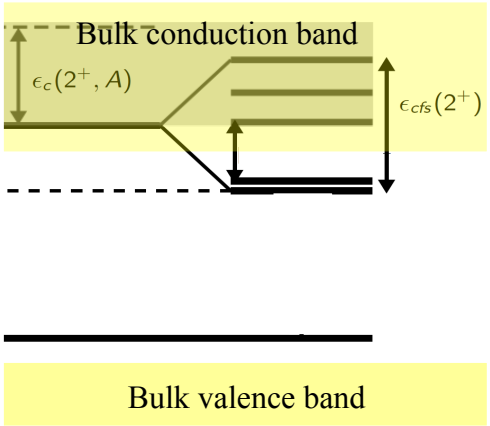
Calculation for the host $Ba_3Si_6O_{12}N_2$

abinit.org

Crystalline structure of host material

↓

Ground state structural relaxation



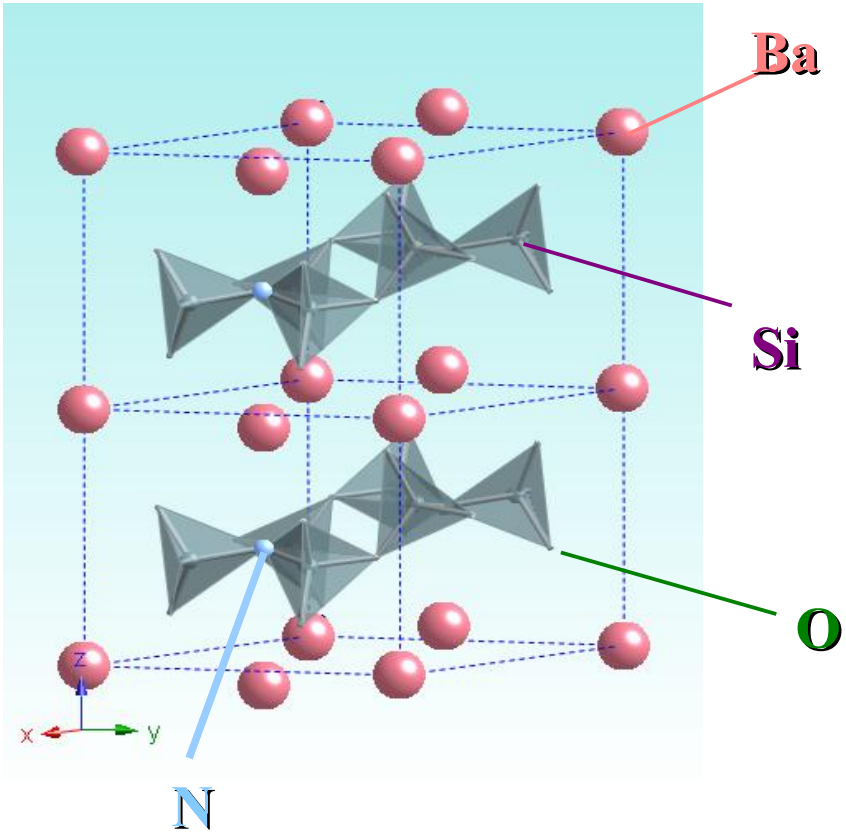
Calculation for $Ba_3Si_6O_{12}N_2 : Eu^{2+}$

New crystal structure for oxynitride

Crystalline structure of $Ba_3Si_6O_{12}N_2$ by Abinit

- Lattice parameters :
  DFT (GGA) with PAW atomic data

	Parameter *a* (Å)	Parameter *c* (Å)
Experimental	7.5046(8)	6.4703(5)
[1] Ba without semi-core states	7.597	6.575
[2] Ba with semi-core states	7.610	6.552



[1] M. Mikami *et al.*, Key Engineering Material Vol. 403 (2009).
[2] M. Mikami, N. Kijima, B. Bertrand, M. Stankovski and X. Gonze, *In press*

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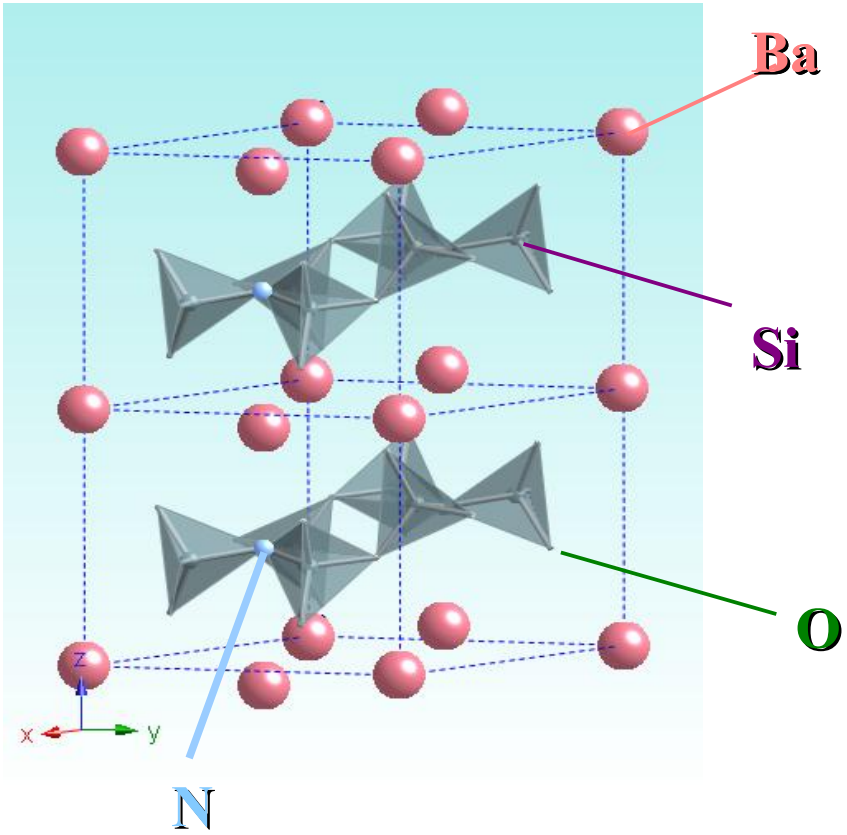
Experimental	7.5046(8)	6.4703(5)
[1] Ba without semi-core states	7.597	6.575
[2] Ba with semi-core states	7.610	6.552

- PAW atomic data for Barium

Results are coherent with experimental data whether semi-core states are used or not



[1] M. Mikami *et al.*, Key Engineering Material Vol. 403 (2009).
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Using abinit : GW + PAW calculation

Calculation for the host $Ba_3Si_6O_{12}N_2$

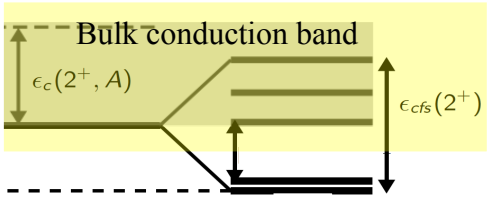
abinit.org

Crystalline structure of host material

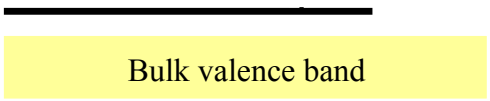
Electronic structure of host material

↓

G_0W_0 + PAW calculation



Calculation for $Ba_3Si_6O_{12}N_2 : Eu^{2+}$



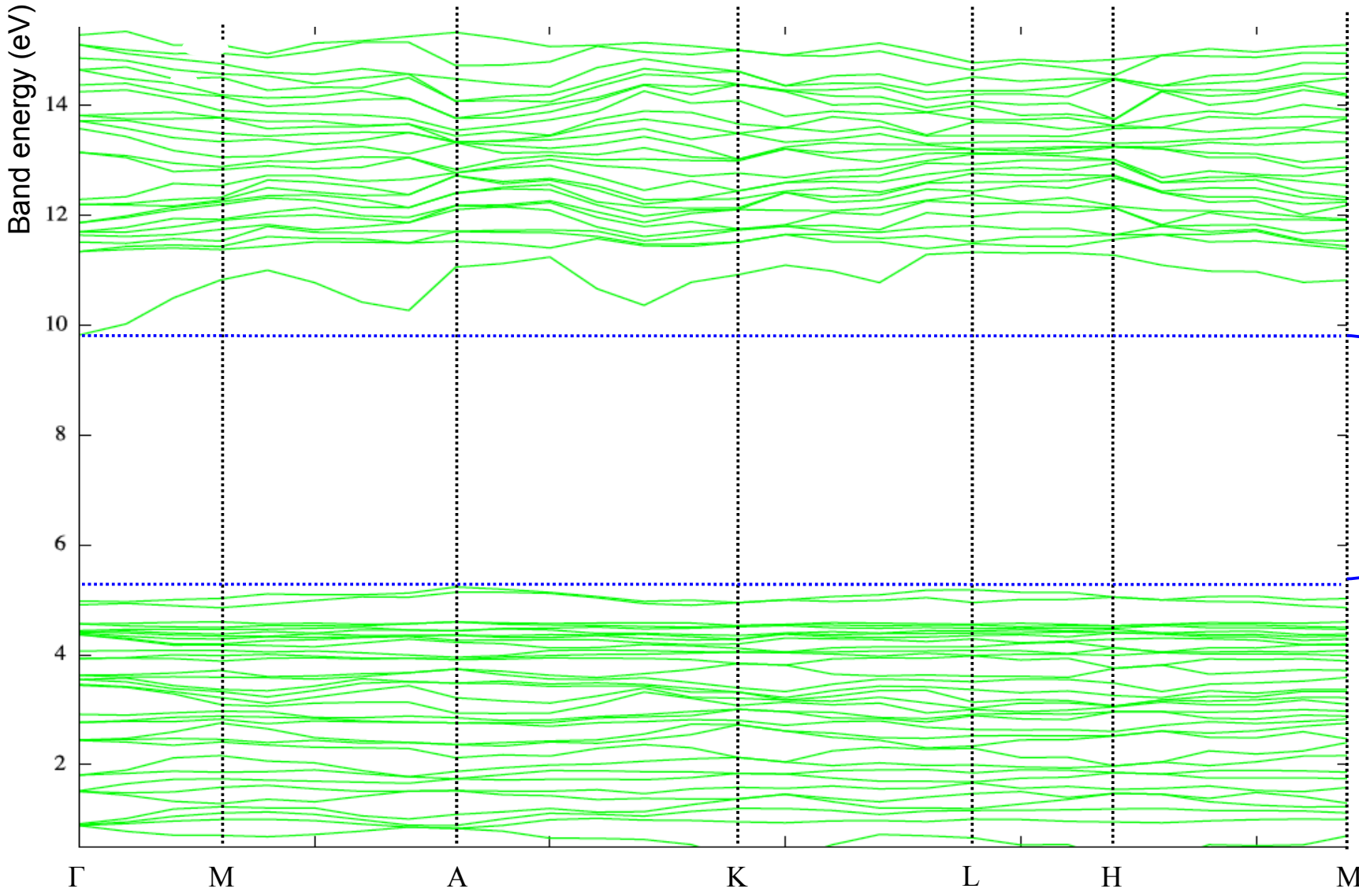
Why is it mandatory to invoke a GW correction ?

Highly covalent oxynitride phosphors

- Large effects of the screening on the optical properties
- Density functional theory (DFT) fails seriously in the description of band gaps or photoemission.
- The standard way to go beyond is to invoke many-body perturbation theory (MBPT).

	DFT indirect gap (eV)	G_0W_0 indirect gap (eV)	Experimental gap (eV)
$Ba_3Si_6O_{12}N_2$	4.589	6.772	7.05 ± 0.25

GW correction to DFT

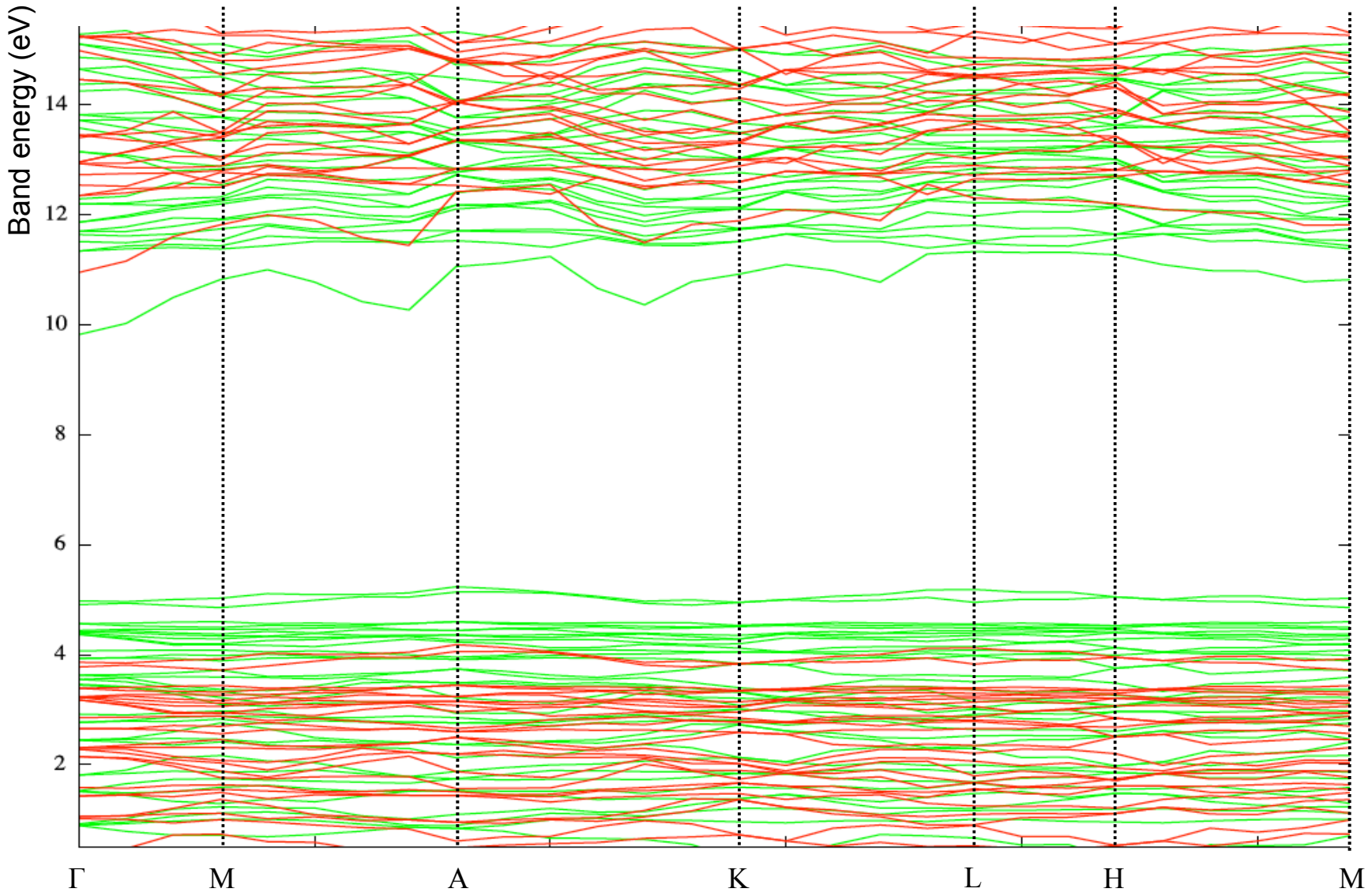


DFT Gap :
4.589 eV

Zoom on the state around the band gap

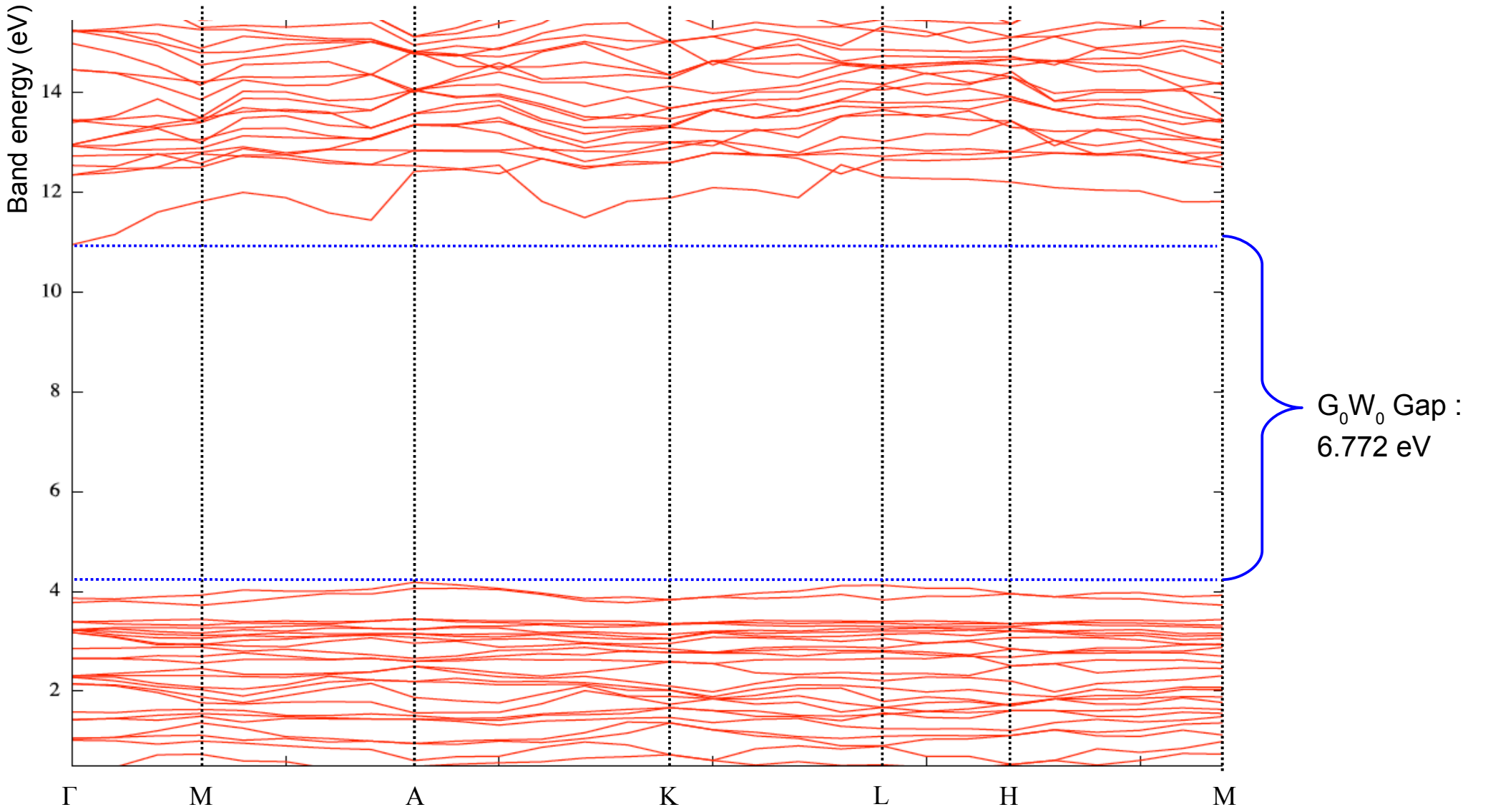
GW correction to DFT

BB

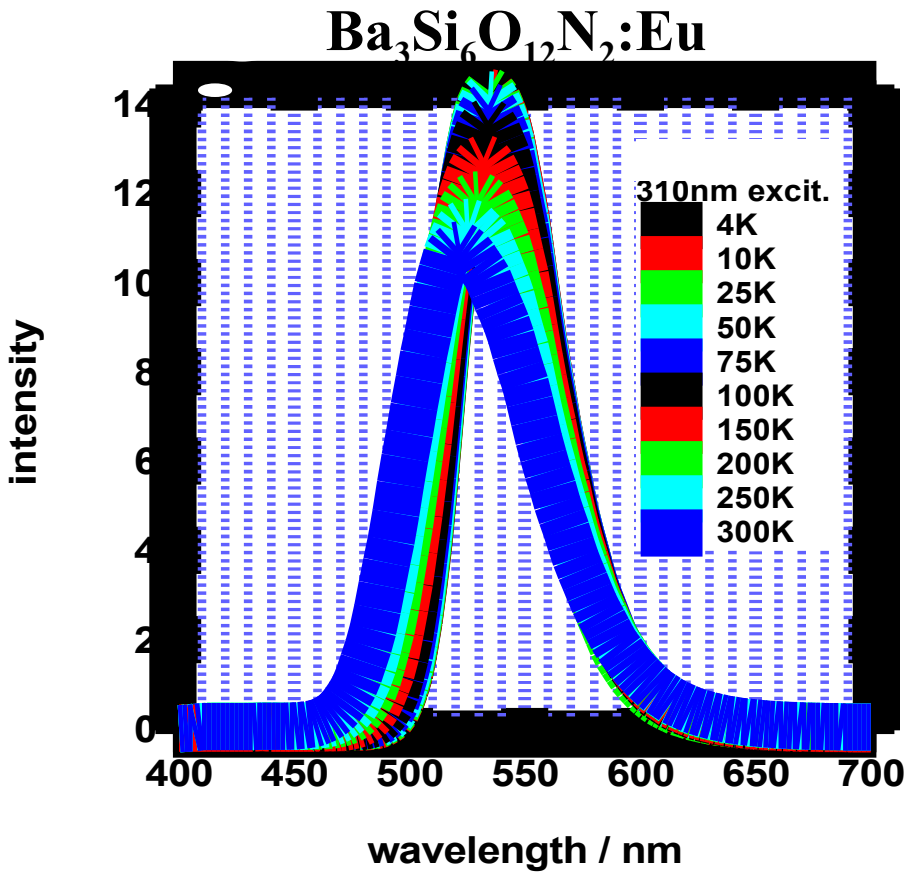


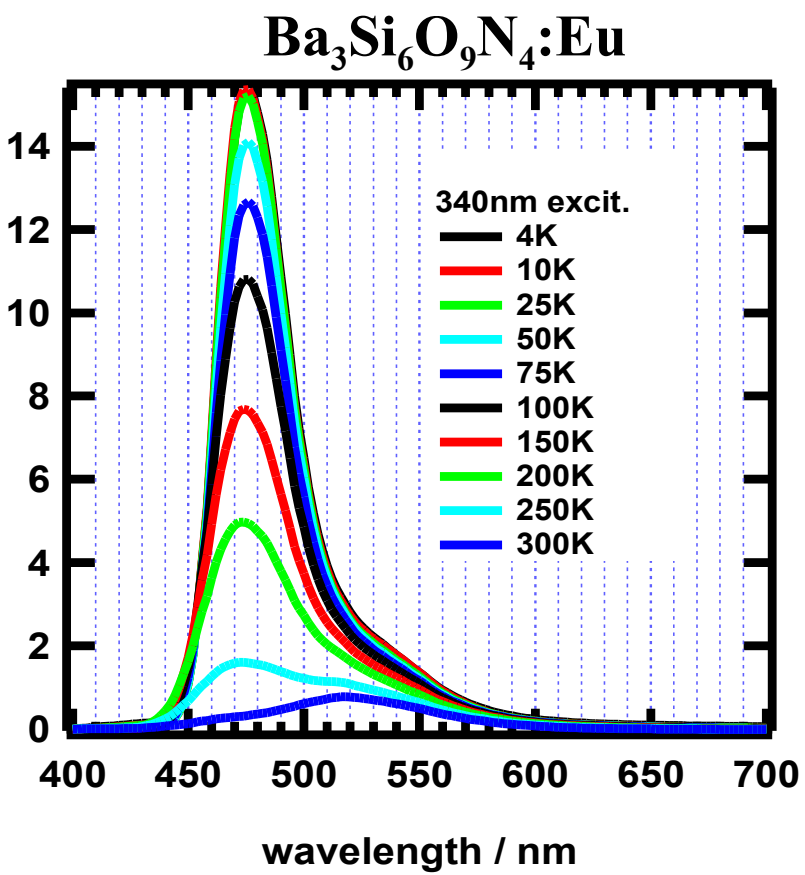
GW correction to DFT

BB



$Ba_3Si_6O_{12}N_2$ / $Ba_3Si_6O_9N_4$ Eu f-d emission





PL peak 530nm (Green)
strong luminescence@R.T.

PL peak 480nm (Blue-green)
quenching @ R.T.

Uheda *et al.* (2007), MM *et al.* (2009); see also, C. Braun *et al.*(2010)

Comparison of energy gaps

- Comparison of materials with similar composition but different thermal quenching

1) $Ba_3Si_6O_{12}N_2$ + Eu^{2+} : Strong luminescence at room temperature
2) $Ba_3Si_6O_9N_4$ + Eu^{2+} : Little luminescence at room temperature

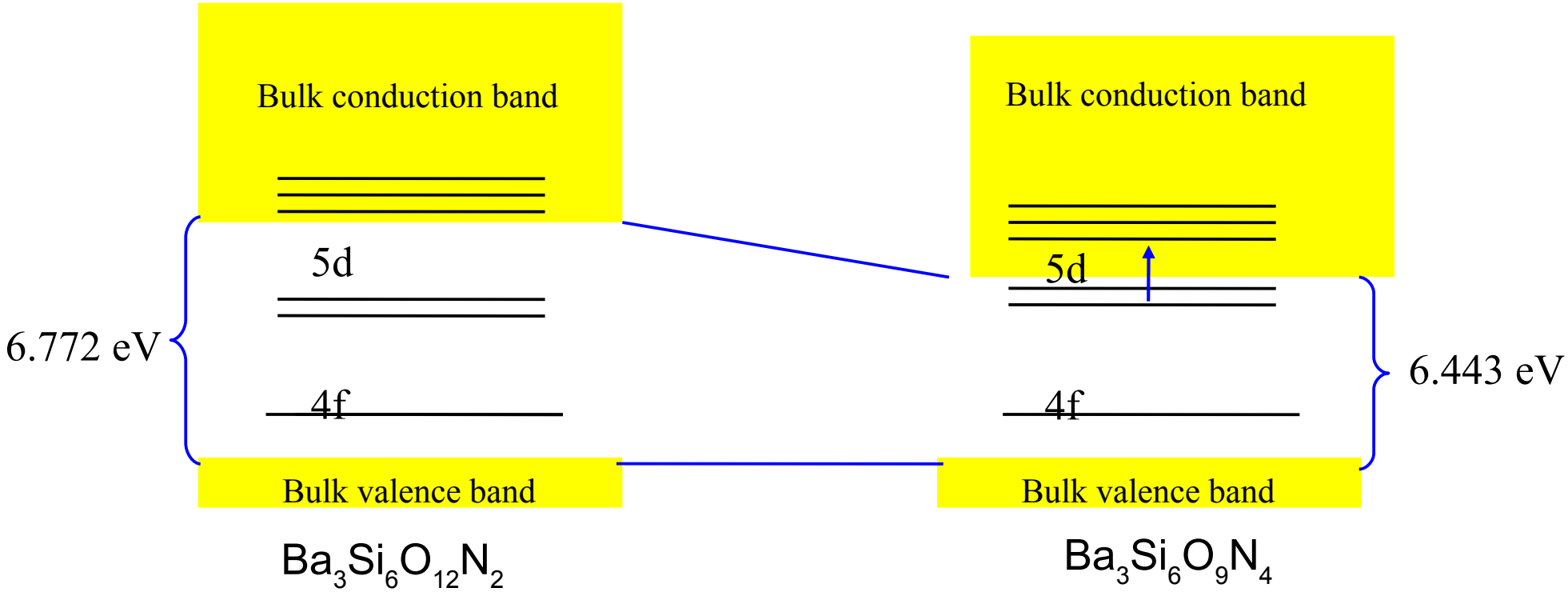
- Our results are in agreement with the auto-ionization model to explain the better thermal properties of $Ba_3Si_6O_{12}N_2$

	GW indirect gap (eV)	GW direct gap at Γ (eV)	Experimental gap (eV)
1) $Ba_3Si_6O_{12}N_2$	6.772	7.092	7.05 ± 0.25
2) $Ba_3Si_6O_9N_4$	6.443	6.698	

$Ba_3Si_6O_{12}N_2$: Grid of 30 k-points with a (controlled) numerical error of 0.06 eV.
$Ba_3Si_6O_9N_4$: Grid of 14 k-points with a (controlled) numerical error of 0.06 eV.

Nband (SCR) : 423
Nband (SIG) : 450
Gwencomp (SCR) : 2.5
Gwencomp (SIG) : 2.0
Ecuteps : 7 Ha
Ecutsigx : 20 Ha

Comparison of energy gap



Calculation for the host $Ba_3Si_6O_{12}N_2$

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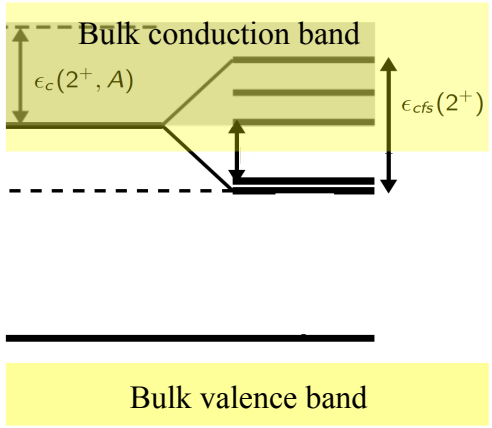
Crystalline structure of host material ⟹ Electronic structure of host material



Calculation for $Ba_3Si_6O_{12}N_2 : Eu^{2+}$

PAW atomic data for Europium

↓

Semi-core states

Construction of PAW atomic data

Semi-core states are required in order to make sensible the G_0W_0 correction.

- Barium Semi-core : $4d^{10}\ 5s^2$
  Valence : $5p^6\ 6p^2$

$Ba_3Si_6O_{12}N_2$	G_0W_0 indirect gap (eV)	G_0W_0 direct gap (eV)
4d semi-core	6.772 Γ - A	7.092 Γ
Without semi-core state	3.740 L - A	3.807 L
Experimental	7.05	

- Europium Semi-core : $4d^{10}\ 5s^2$
  Valence : $5p^6\ 4f^7\ 6p^2$

Test of the G_0W_0 correction to EuO : - Introduction of semi-core $4d^{10}$ states

-

Problems with the correction of 4f states

Calculation for the host $Ba_3Si_6O_{12}N_2$

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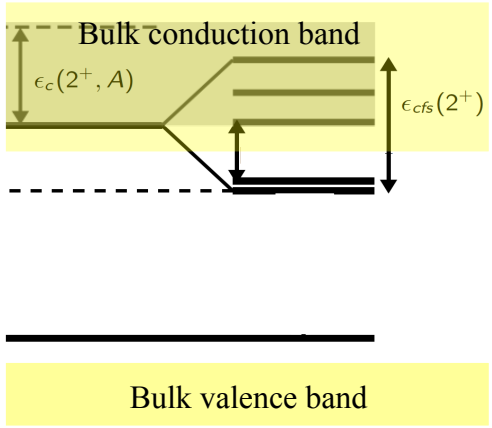
Crystalline structure of host material ⟹ Electronic structure of host material



Calculation for $Ba_3Si_6O_{12}N_2 : Eu^{2+}$

Position and concentration of Eu impurities

↓

Spin polarized GGA(+U)

⟺ PAW atomic data for Europium

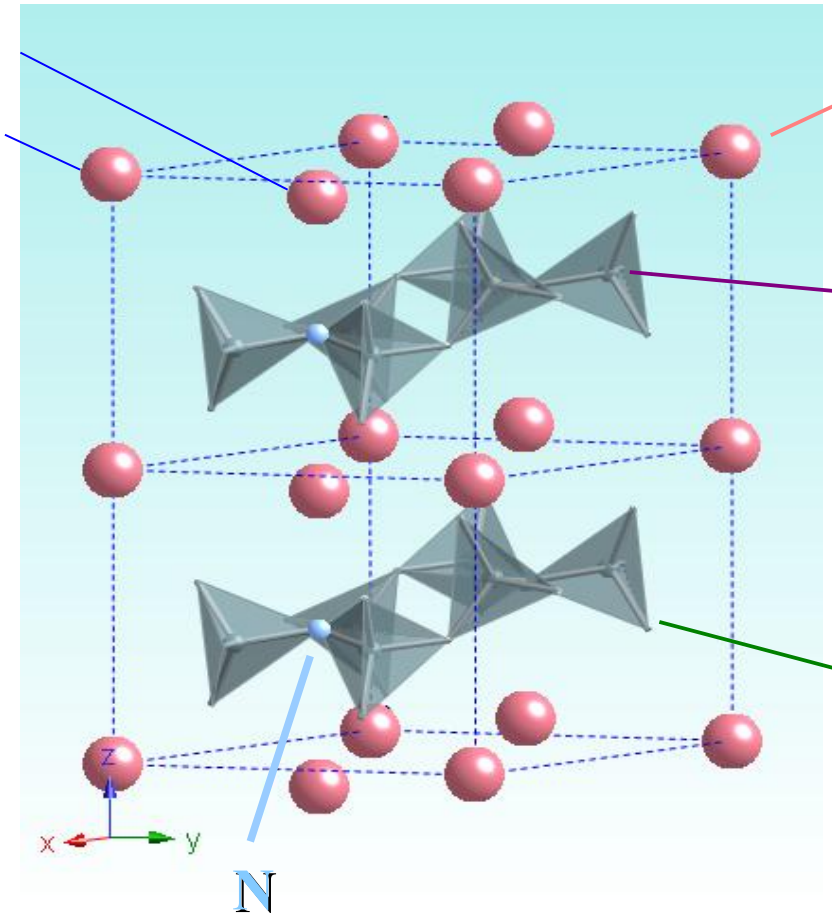
Adding Europium impurities

Eu impurities act as luminescence centers

Ba-(O,N) or Eu-(O,N)

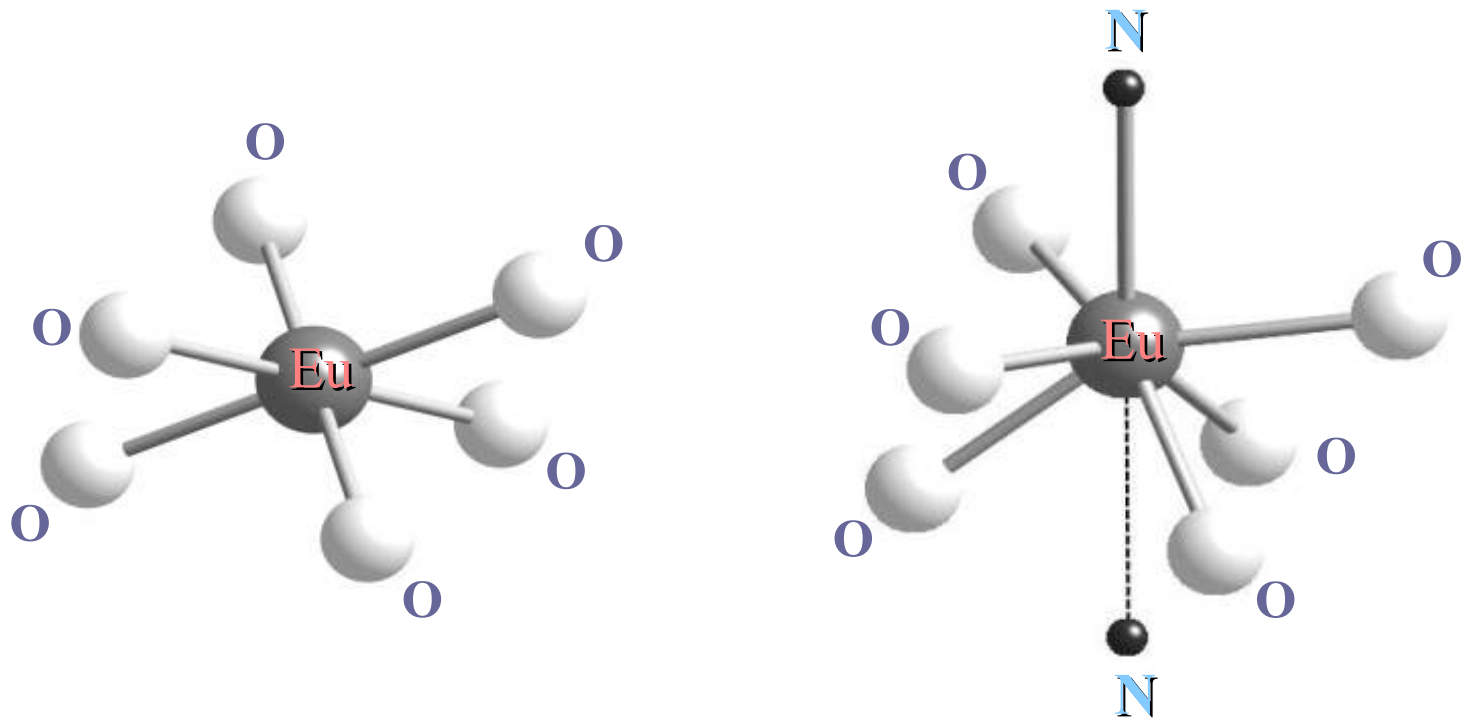
Ba-(O) or Eu-(O)

Onxynitride layer :
SiO_3N tetrahedra



Non equivalent positions

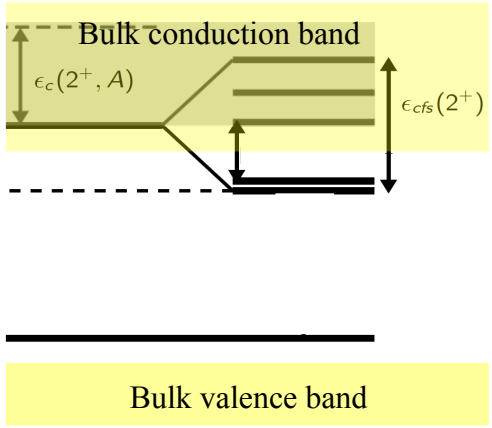
Europium substitutes to Barium atoms in two possible non equivalent positions



Using abinit : Perspectives

Calculation for the host $Ba_3Si_6O_{12}N_2$

Crystalline structure of host material ⟹ Electronic structure of host material



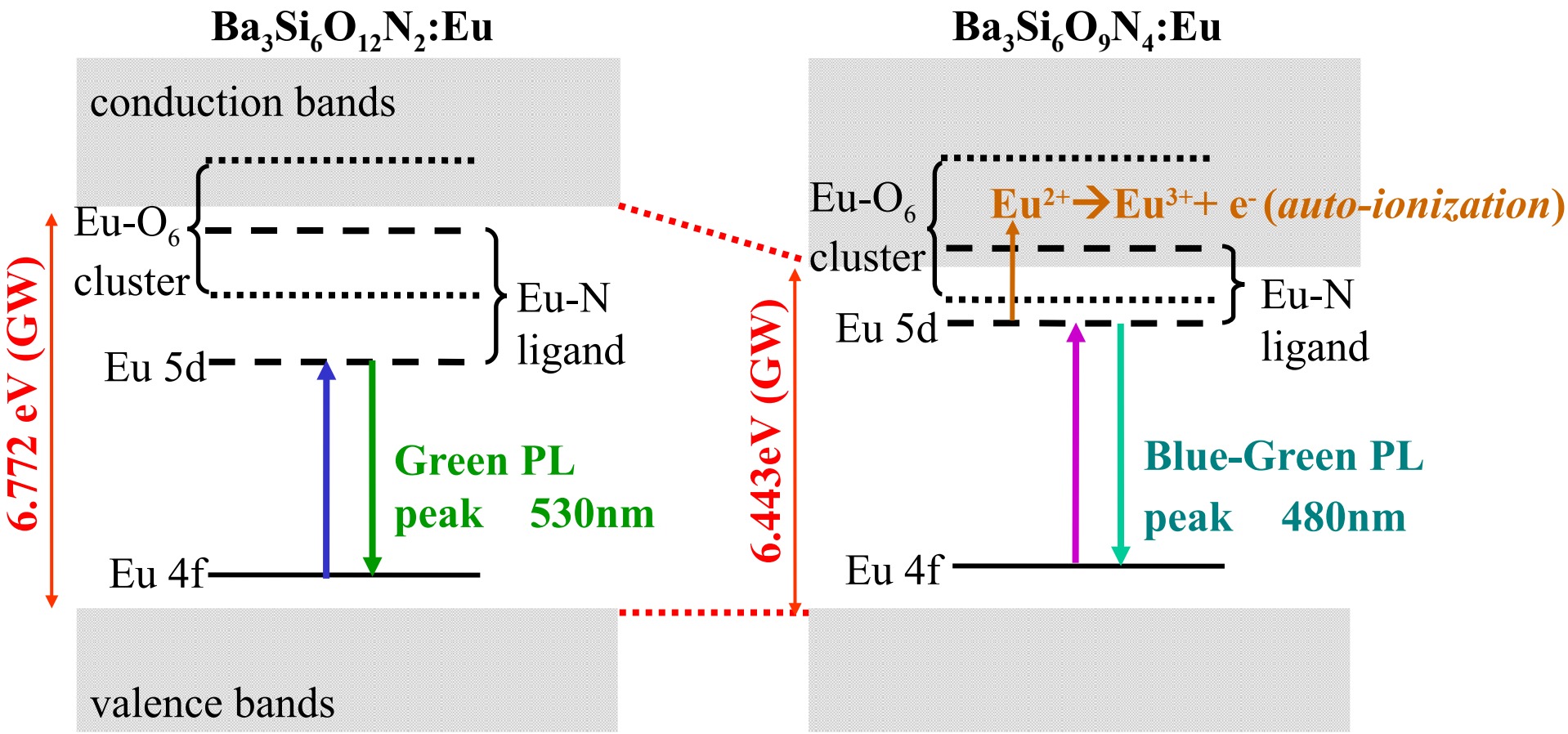
Calculation for $Ba_3Si_6O_{12}N_2 : Eu^{2+}$

Perspective :

Position of the 4f and 5d states of Europium ⟺ Position and concentration of Eu impurities ⟺ PAW atomic data for Europium

The difference of EU PL : a model

MM



proposed by MM *et al.*(2009): based on Dorenbos scheme (J.Phys.Cond.Mat.17, 2005)

Towards a validation of the model

$Ba_3Si_6O_{12}N_2$:Eu

conduction bands

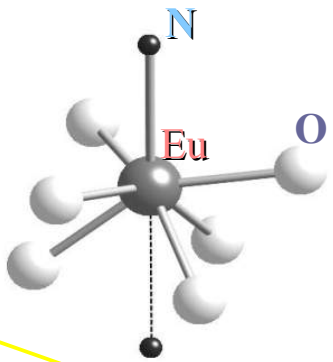
Eu-O_6 cluster

Eu-N ligand

Eu 5d

Eu 4f

valence bands



Zoom on the bottom of the conduction band - Preliminary results

Conclusion

New crystal structure for oxynitride

BB

Business through Innovation

- **Scientific interest**

  Luminescence properties of rare-earth doping oxynitrides phosphors

  - Emission and absorption spectra
  - Thermal quenching

ETSF

- **Numerical Challenge**

  Electronic structure of $Ba_3Si_6O_{12}N_2$ phosphor

  - Current : G_0W_0 with PAW atomic data including semi-core and 4f states
  - Future : Electron-phonon interaction

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- **Industry ► Reducing the cost of R&D**
  - Discovery of new compounds
  - Prediction of properties before synthesis

MITSUBISHI CHEMICAL

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A photo from Sendai (Tohoku University)

"Prof. Kotaro Honda in Director office is keeping up even after breakdown of the table by Tohoku-Pacific Ocean Earthquake on March 11 2011"