First-principles study of phosphors for white-LED applications

X. Gonze
Université catholique de Louvain, Belgium
and
Skolkovo Institute of Technology

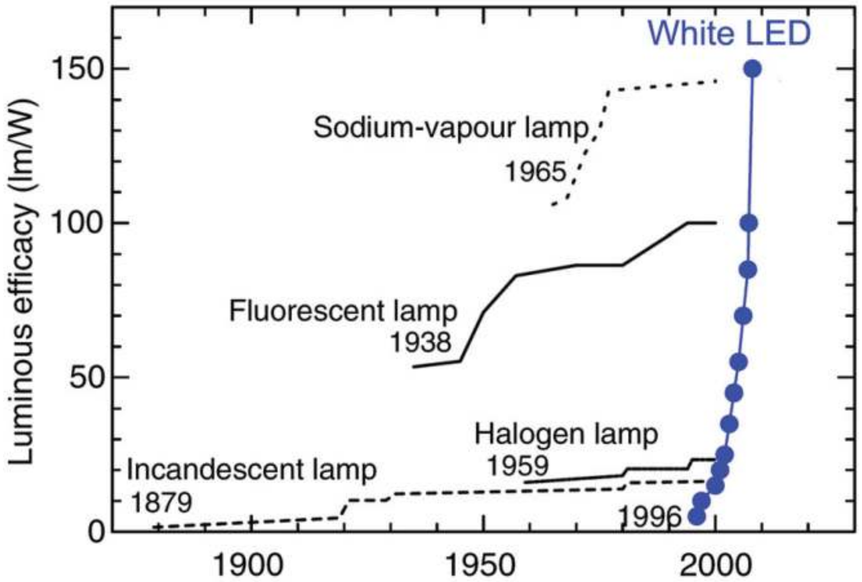
Collaborators :
Y. Jia, J. Bouquiaux, A. Miglio, M. Giantomassi, U.C. Louvain, Belgium
S. Poncé, EPFL, Switzerland
M. Mikami, Mitsubishi Chemical HC, Japan

Supported by the Russian Scientific Foundation grant No. 19072-30043
"Computational materials design laboratory"

Moscow, November 11, 2020

Lighting : energy consumption ...

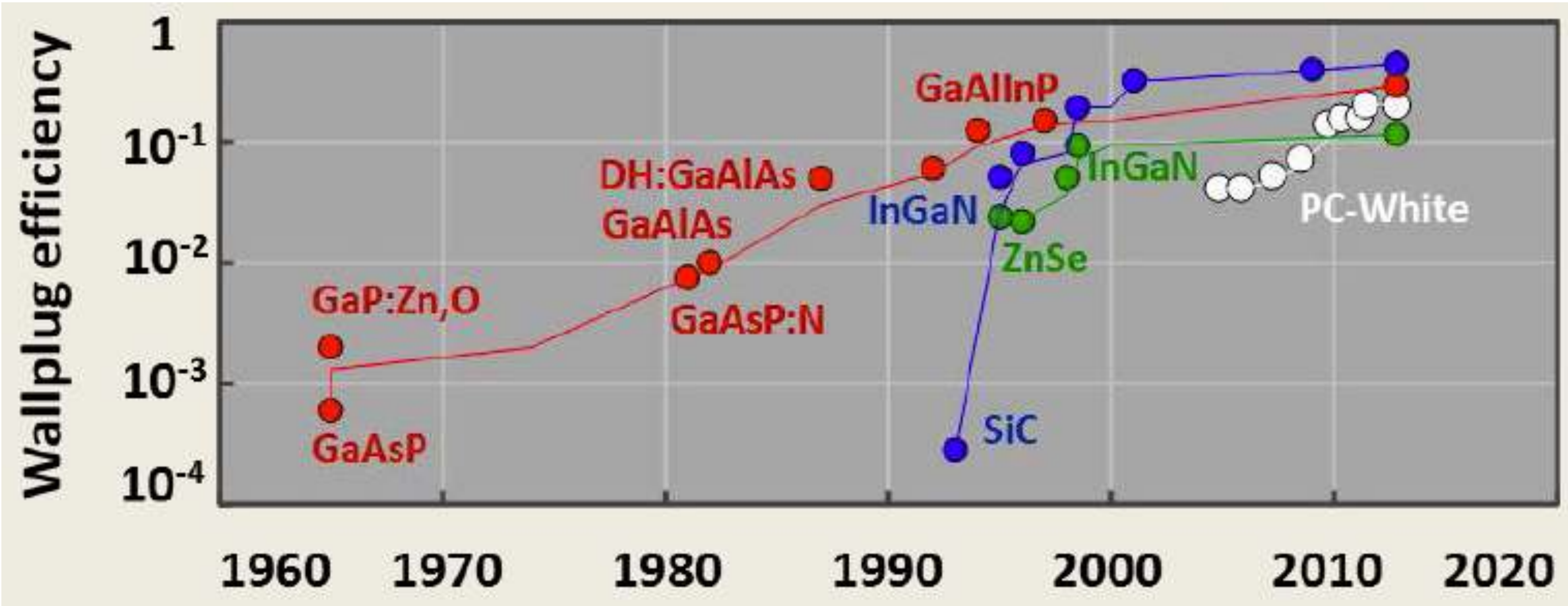
"Lighting represents almost 20% of global electricity consumption. This consumption is similar to the amount of electricity generated by nuclear power." *(Int. Energy Agency)*



lm = Lumen = SI unit for the total *visible* flux emitted by a source
Includes luminosity function ; 1 W of green light (555 nm) => 683 lm

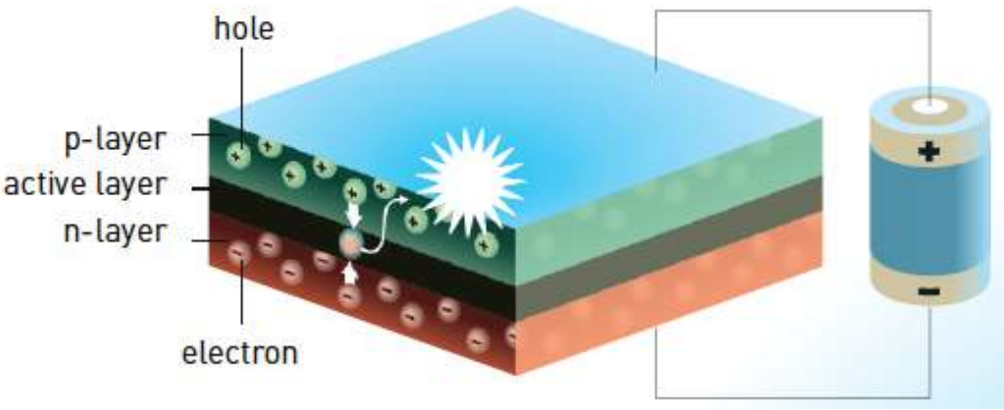
Efficiency of light-emitting diodes : decades of improvements

Red … blue ... Nobel prize in physics 2014 Akasaki, Amano, Nakamura
+ phosphor => PC-White : Phosphor converted white-light

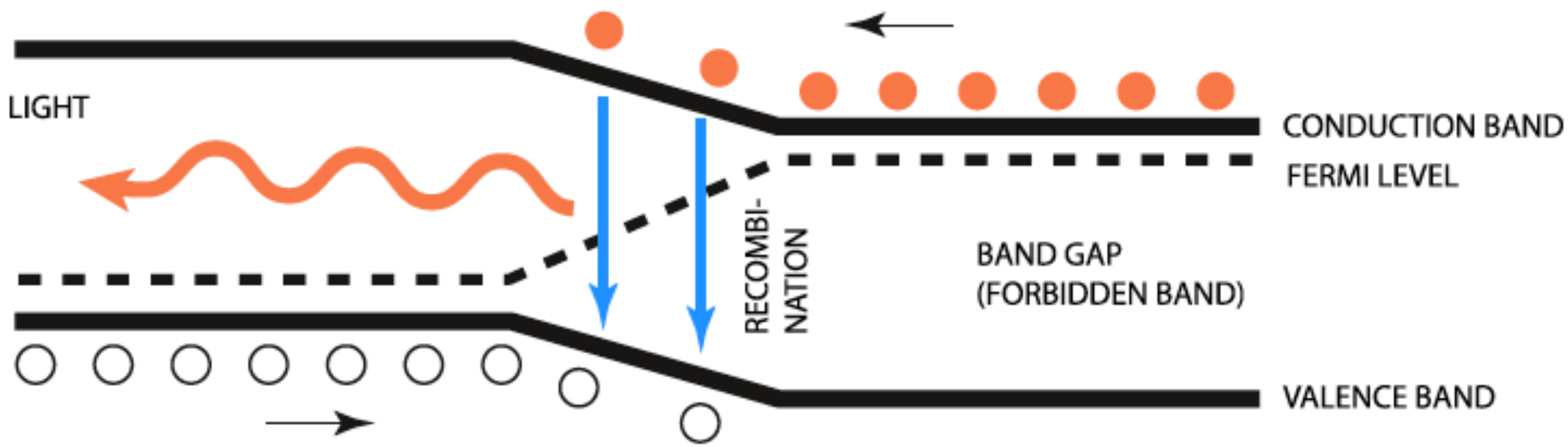


Wall plug efficiency : ratio between electrical power (in) and optical power (out)

Electroluminescence : Light-emitting diode

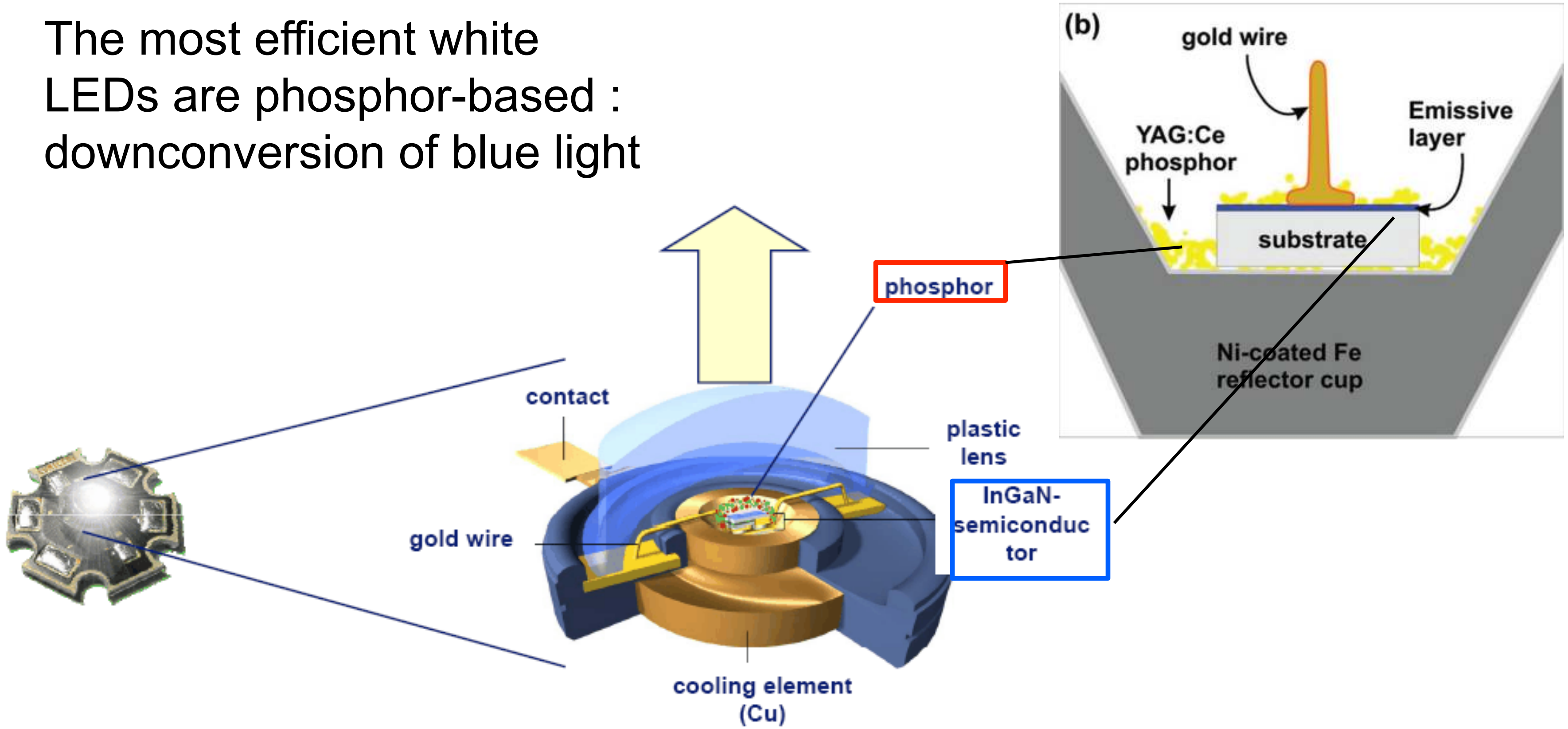


Applying an adequate difference of potential inject holes in the p-region and electrons in the n-region
=> electron-hole pairs



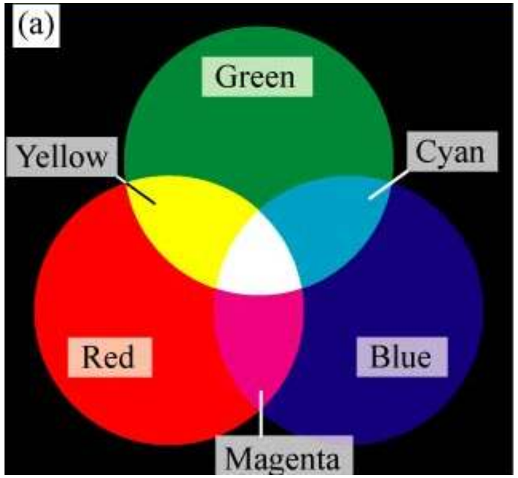
Standard white PC-LED

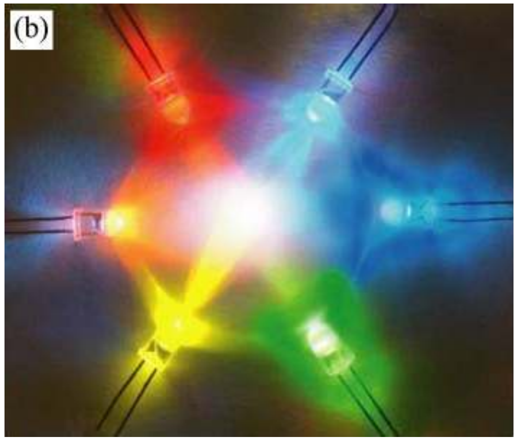
The most efficient white LEDs are phosphor-based : downconversion of blue light



(In, Ga)N semiconductor chip + phosphors		White light
Blue chip, 420-480 nm	yellow phosphor	cool white
Blue chip, 420-480 nm	R+G phosphor blends	warm white

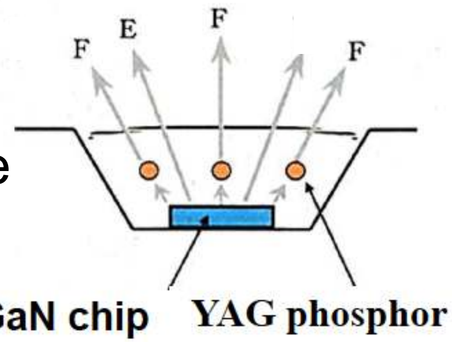
Blue+yellow LED emission spectrum

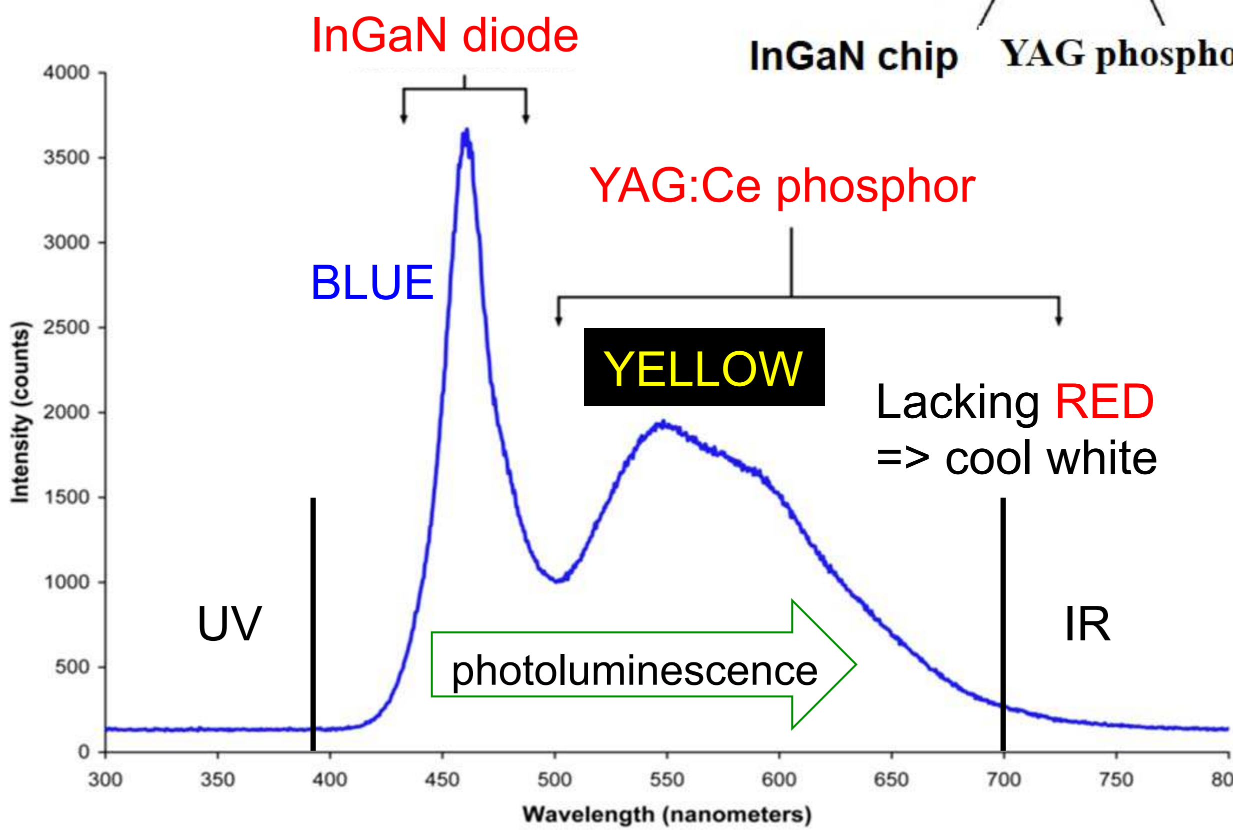




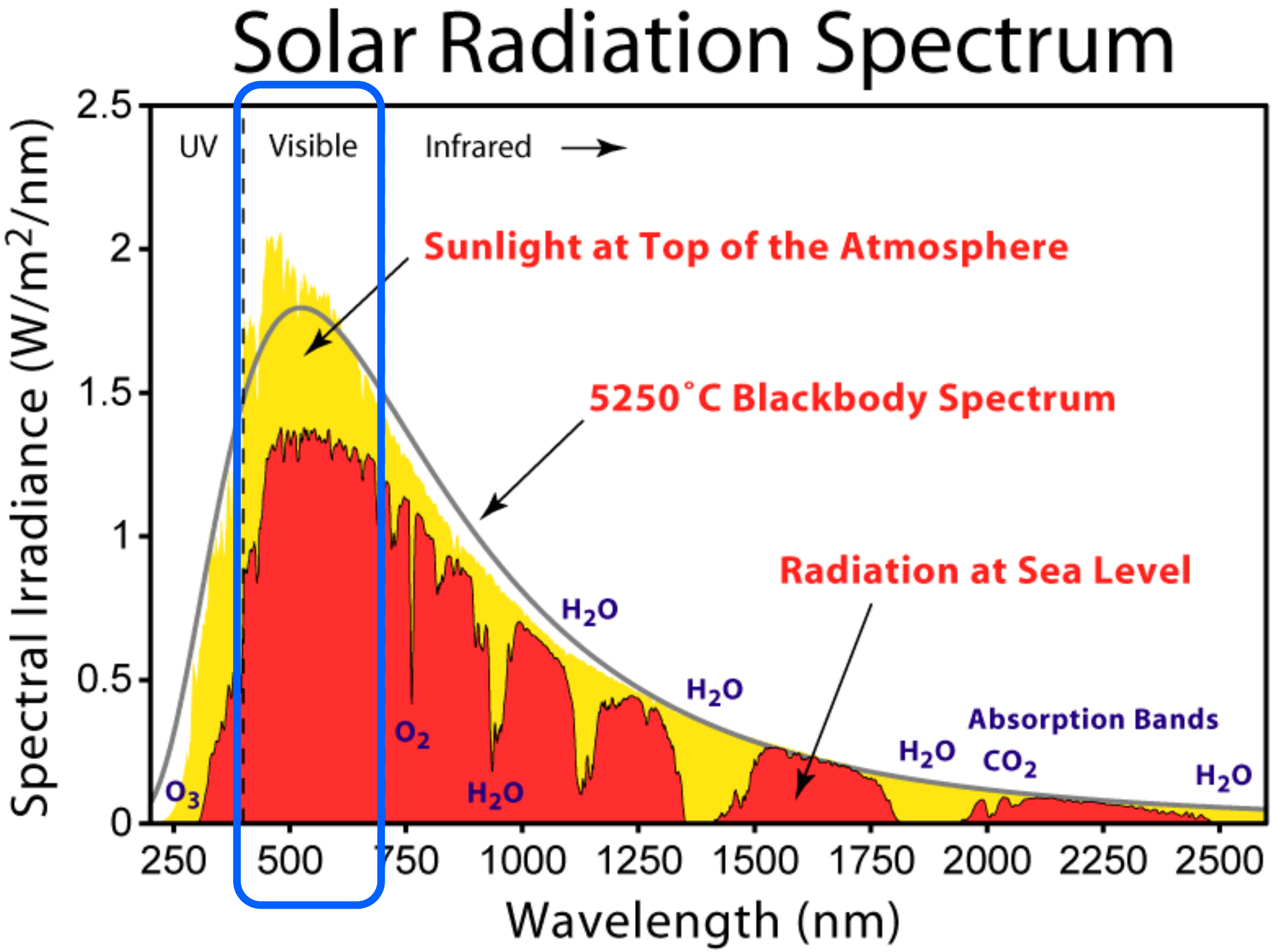
Downconversion of blue light

by Yttrium Aluminum Garnet : Ce





Compare with solar spectrum



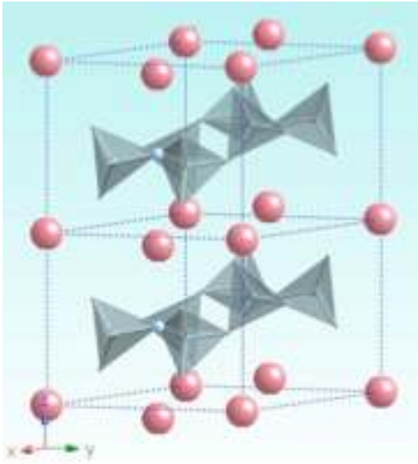
Wide diversity of LED+phosphors

Conventional type Blue-LED + yellow phosphor
(typically, $Y_3Al_5O_{12}:Ce^{3+}$)

High color rendering types Blue-LED + yellow & red
Near UV-LED + blue & green & red
Blue-LED + green & red

Tab. 1.3 Spectral position of the emission band of Eu^{2+} in some representative lattices.

SrB_4O_7:Eu	368 nm
$Sr_2P_2O_7$:Eu	420 nm
$BaMgAl_{10}O_{17}$:Eu	453 nm
$Sr_4Al_{14}O_{25}$:Eu	490 nm
Ba_2SiO_4:Eu	505 nm
$SrGa_2S_4$:Eu	535 nm
Sr_2SiO_4:Eu	575 nm
SrS:Eu	615 nm



Phosphor tuning ? Host/dopant ? Selection criterion ?

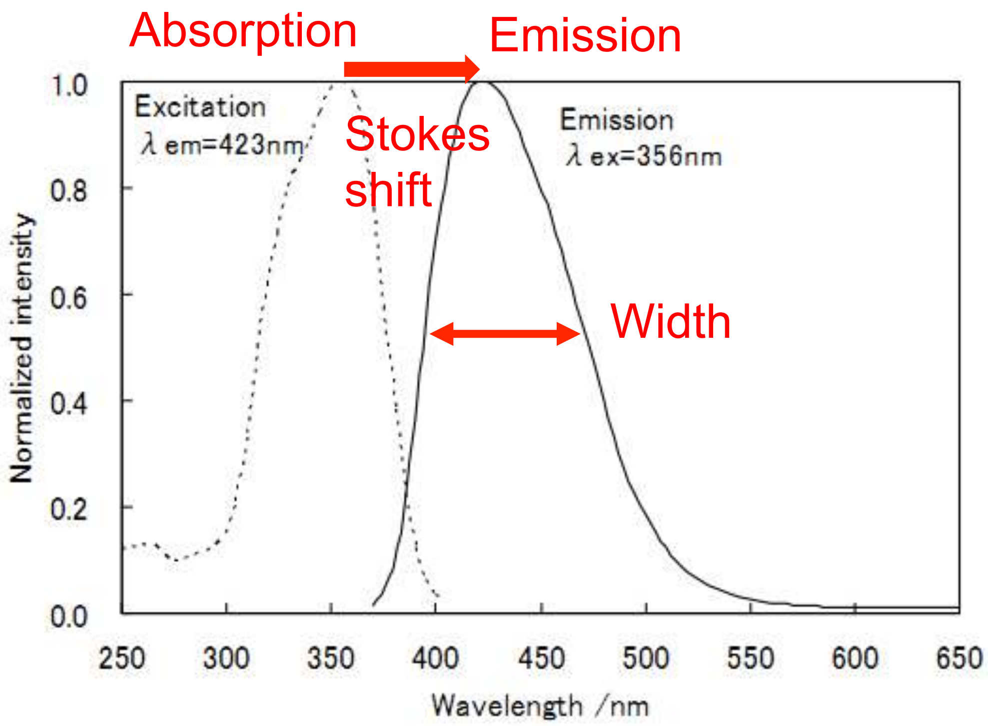
Overview

1. Role of phosphors in white-LEDs
2. Working principles, selection criteria, 4f-5d phosphors
3. How to model ? First-principles ... but not too much !
4. Theoretical study of lanthanum silicon nitrides hosts + Ce
5. Scaling up : results for 28 different hosts
6. Thermal quenching, width of emission, beyond 1D model

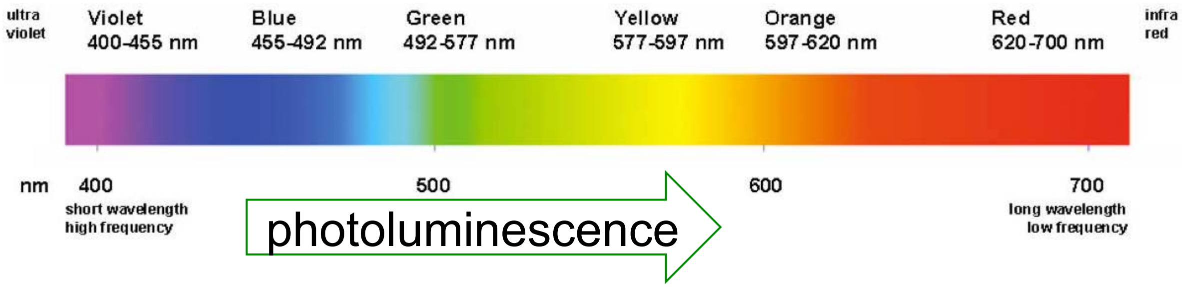
References :

Y. Jia, A. Miglio, S. Poncé, X. Gonze and M. Mikami, *Phys. Rev. B* **93** 155111 (2016)
X. Gonze *et al, Comput. Phys. Commun.* **205**, 106 (2016)
Y. Jia, A. Miglio, S. Poncé, M. Mikami and X. Gonze, *Adv. Opt. Materials*, 5, 1600997 (2017)
Y. Jia, A. Miglio, S. Poncé, M. Mikami and X. Gonze, *Phys. Rev. B* 96, 125132 (2017)
Y. Jia, A. Miglio, M. Mikami and X. Gonze, *Phys. Rev. Mat.* 2, 125202 (2018)
Y. Jia, A. Miglio, S. Poncé, M. Mikami and X. Gonze, *Phys. Rev. B* 100, 155109 (2019)
J. Bouquiaux, Y. Jia, S. Poncé, A. Miglio, M. Mikami & X. Gonze, *arXiv:cond-mat.mtrl-sci 2010:00423 (2020)*
+ Review on phosphors :
P. F. Smets, A. B. Parmentier and D. Poelmans
"Selecting Conversion Phosphors for White Light-Emitting Diodes"
J. Electrochemical Society **158** R37 (2011)

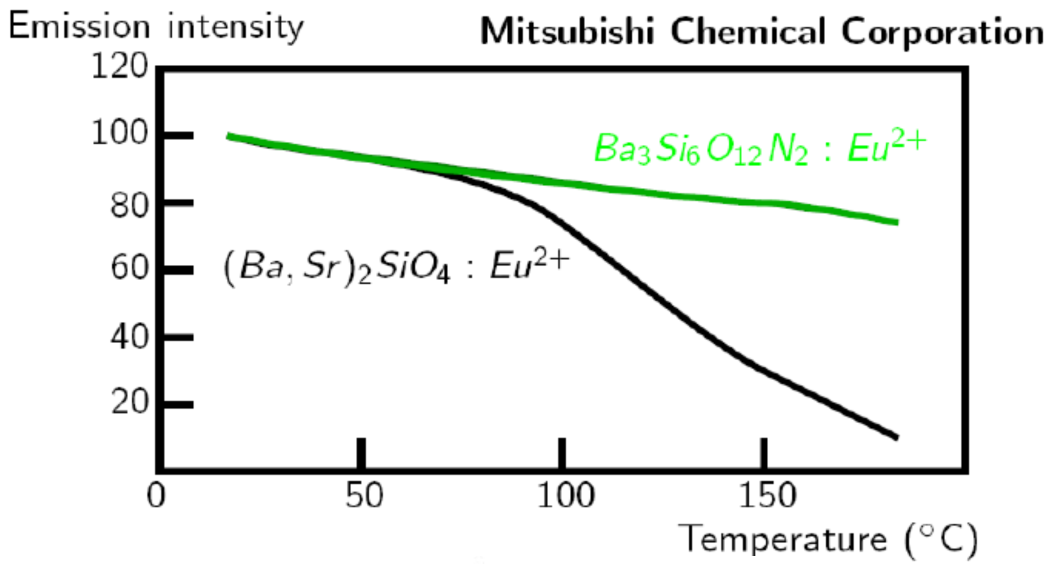
Absorption/emission/Stokes shift

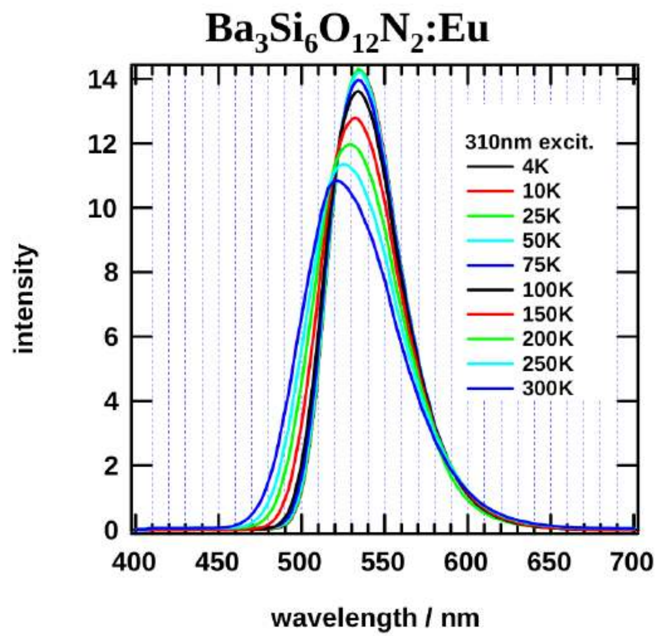


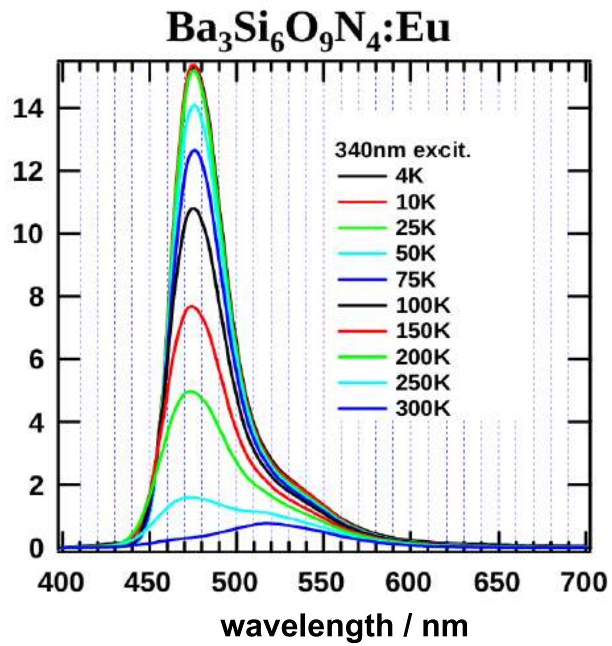
(1) Absorption occurs
(2) Atomic configuration changes, decreasing the energy
(3) Emission occurs



Thermal quenching







See e.g. C. Braun … W. Schnick, Chem. Eur. J. 16, 9646 (2010)

Criteria for selecting phosphors

1. Emission spectrum that complements adequately the LED (+ other phosphors if use more than one)
   Importance of linewidth (missing: good red narrow width phosphor)

2. Excitation spectrum with good overlap with the pumping LED, and large absorption strength

3. Optical characteristics unchanged at elevated temperature (450K)

4. Quantum efficiency approaching unity

5. Chemical stability

6. Absence of emission saturation at high fluxes

Ce- and Eu- doped inorganic hosts

Best choice (at present) :

Ce^{3+} and Eu^{2+} - doped « inorganic hosts » : 4f – 5d transition

[ternary/quaternary silicates, phosphates, (oxy)nitrides, (oxy)sulfides, etc]

Ce and Eu substitutional to trivalent or divalent ions

Large absorption strength

Excellent quantum efficiency (>90% for YAG:Ce)

Tunable

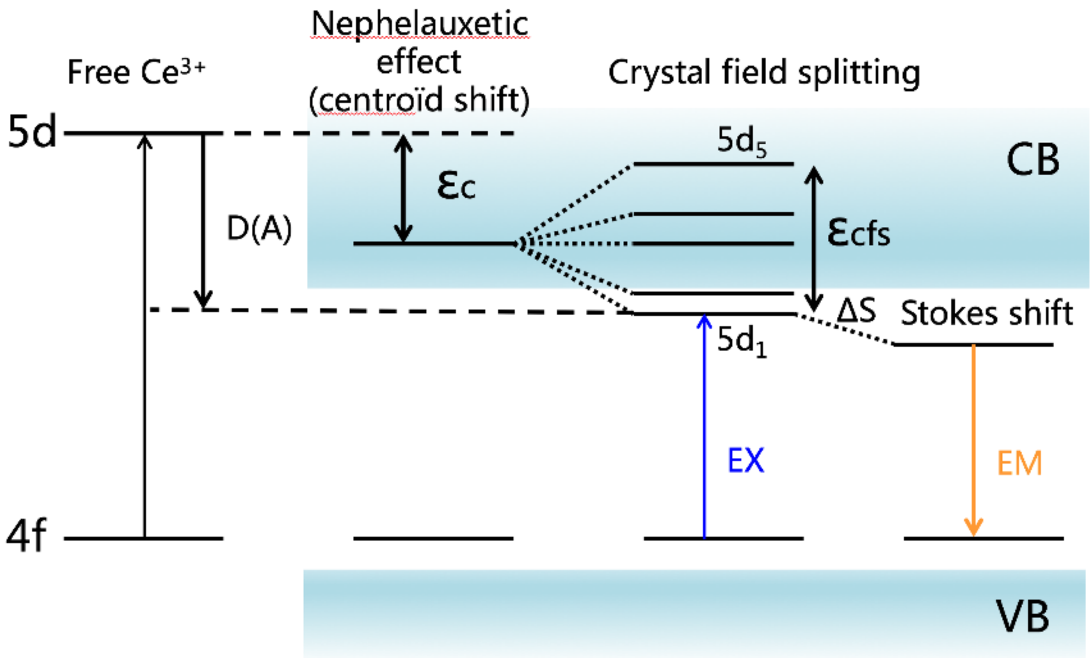
But : Thermal quenching ? Adequate emission band ?

How can theory help for such complex materials ?

High-throughput search, but which indicators ?

Dorenbos model for 4f – 5d transition

Ce (Xe) $4f^2 5d^0 6s^2$ Ce^{3+} (Xe) $4f^1 5d^0 6s^0$ Eu (Xe) $4f^7 5d^0 6s^2$ Eu^{2+} (Xe) $4f^7 5d^0 6s^0$



$$D(A) = \varepsilon_c(A) + \frac{\varepsilon_{cfs}(A)}{r(A)} - 1890cm^{-1}$$

$$\varepsilon_c(A) = 1.44 \times 10^{17} \Sigma_{i=1}^{N} \frac{\alpha_{sp}^i}{R_i^6}.$$

$$\alpha_{sp} = \alpha_0 + \frac{b}{\chi^2}$$

$$\varepsilon_{cfs} = \frac{\beta}{R_{av}^2}$$

Depend on type of coordination incl. # NN

$$E(A) = 49340cm^{-1} - D(A)$$

4f – 4f transitions :
- do not show as nice a tunability
- narrow absorption range => colour drift with T

Dorenbos, PRB, 62, 15640 (2000)
Dorenbos, PRB, 62, 15650 (2000)
Dorenbos, PRB, 64, 125117 (2001)
Dorenbos, PRB, 65, 235110 (2002)
Liu et al, J. Lumin, 166, 106 (2016)

How to model ?
First-principles ...
but not too much !

Search for better phosphors

- Empirical or semi-empirical search (cf Dorenbos)

  exp. data (e.g. emission) for >100 doped hosts

  ? quality of material

  ? data for linewidth, thermal quenching

- Machine-learning based on such exp. data ?
- First-principles :

  either give new data for machine-learning (need accuracy)

  or allow direct high-throughput search (need speed)

Challenge for first-principles

- Optical excitations => electron-hole interaction !
- Bethe-Salpether equation (BSE) ?!
- Supercells - 60 ... 120 atoms (Eu, Ce 6.25% - 12.5%)
- Ce, Eu => 4f electrons !
- “Big”cells : cannot afford BSE
- Need to relax the geometry !
- Simpler approaches to generate indicators ?

Ground state only ? Doped ? Bulk undoped ?

… And how address linewidth ?

… Thermal quenching ?

Indicators : speed vs accuracy

Accuracy

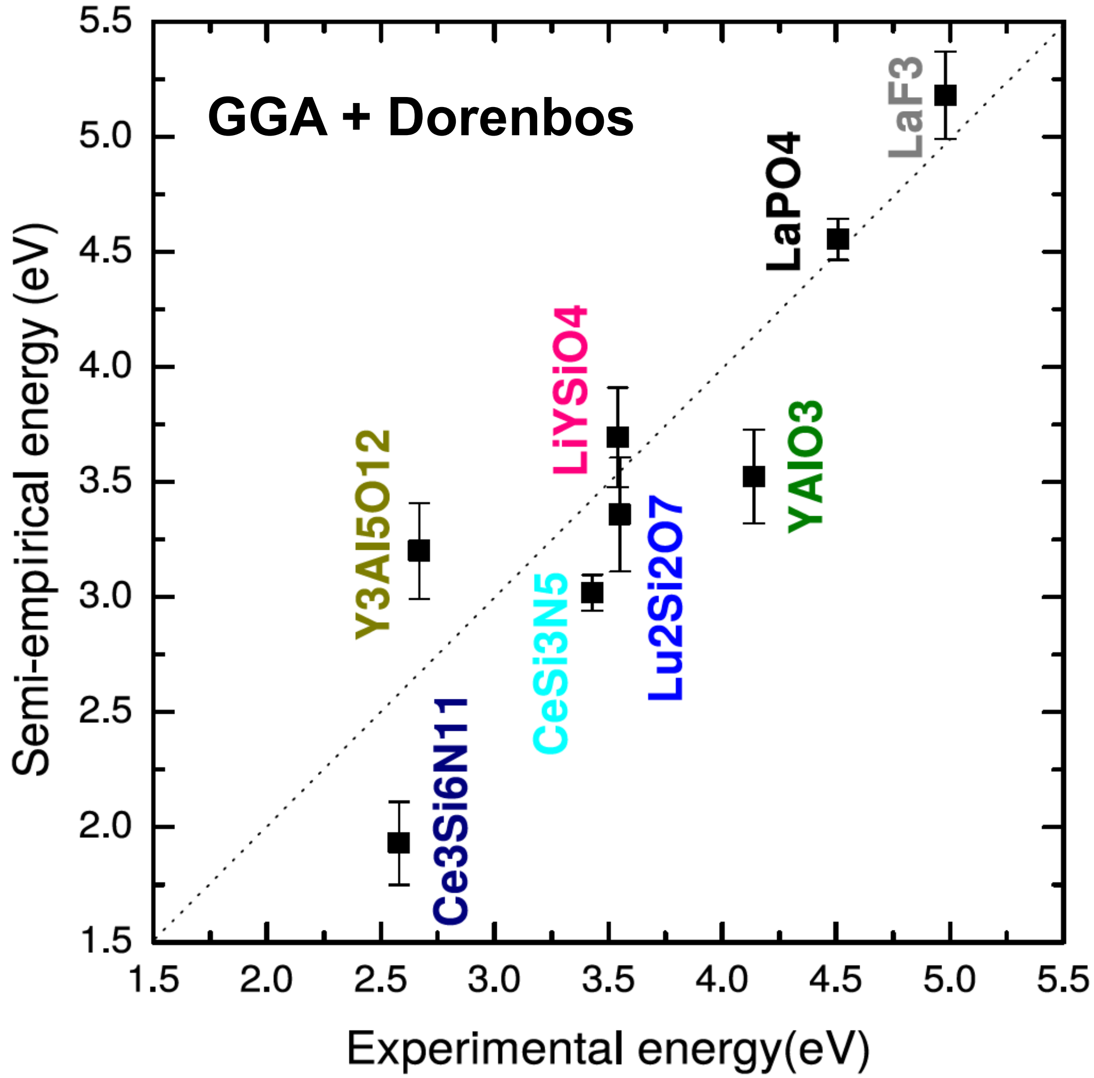
Bethe-Salpeter Equation
(+ geometry relaxation)

Doped ground-state + Dorenbos model

Undoped bulk

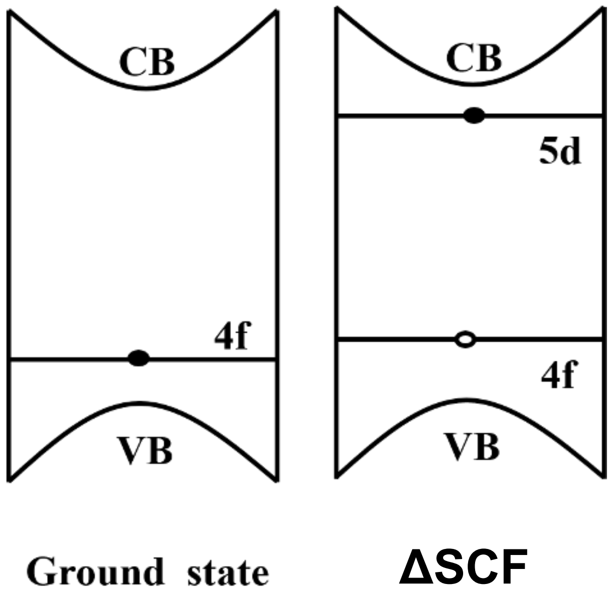
Speed

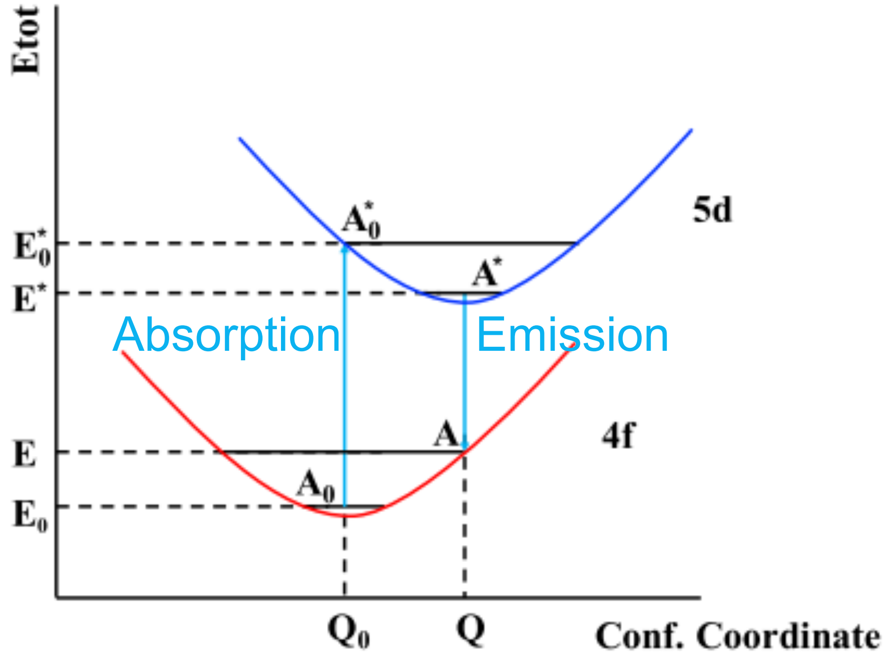
Absorption: GGA + Dorenbos model



Still :
How to predict emission ?
What is the excited state geometry ?

ΔSCF method





Configuration diagram

- ΔSCF method: mimic the interaction between electrons and a 4f-hole. Comparison of total energies of ground and excited states.
- Calculate transition energy based on configuration coordination diagram

  (Seitz 1938, Mott 1938, Gurney 1939 …).

For scintillator absorption see also : Chaudhry, Canning et al,
PRB 83, 125155 (2011), JAP 109, 083708 (2011), PRB 89, 155105 (2014)

Indicators : speed vs accuracy

Bethe-Salpeter Equation
(+ geometry relaxation)

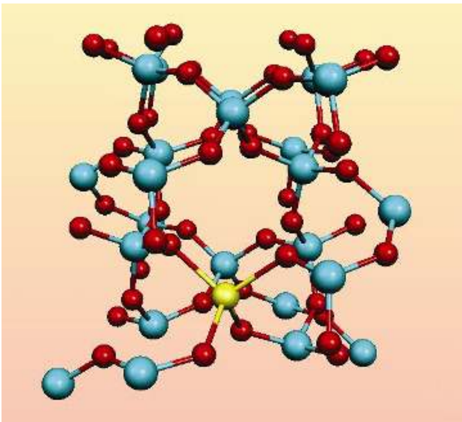
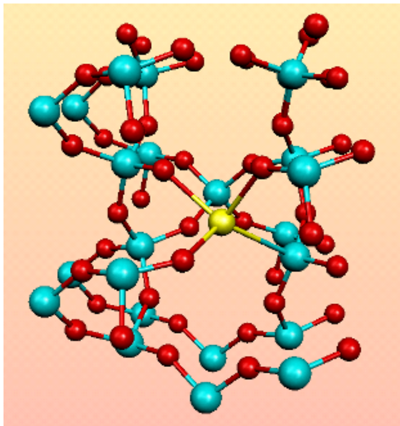
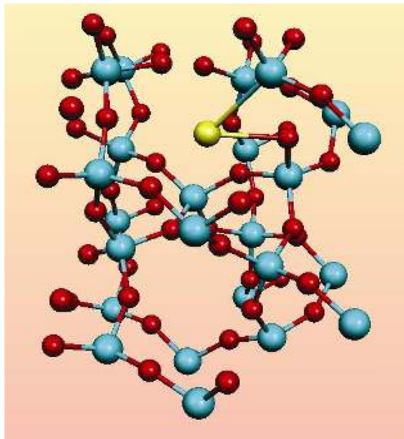
ΔSCF with 1D configuration diagram

Doped ground-state + Dorenbos model

Undoped bulk

First-principles calculations

- Density functional theory (DFT) +U => **Total energy + bands**
- Abinit software (http://www.abinit.org)
- Projector Augmented Wave (PAW) + Plane Waves
- Cutoff energy: 30Ha
- Supercells - 60 ... 120 atoms (Eu, Ce 6.25% - 12.5%)

ABINIT software project

Implementing Density-Functional Theory + Many-body Perturbation Theory.
For solids and nanosystems, computation of :

energetics, electronic structure, vibrations, dielectric responses, optic, Raman, thermodynamics, ...

1997 Ideas :

1) Target a wide range of capabilities => need a worldwide collaboration
2) Linux software development : 'free software' model

1997... 2019 Development :

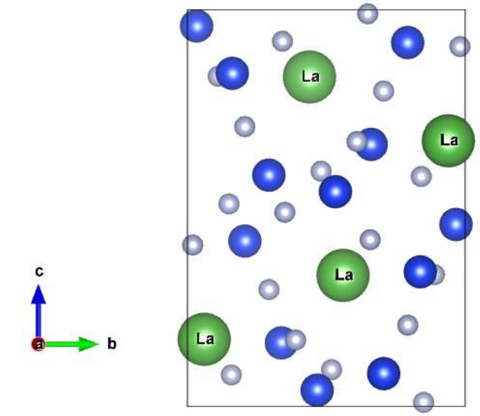
Releases of ABINIT (v1.0.0 to v8.10.2)
8 international ABINIT developer workshops (40 ... 60 participants)

2019 Assessment :

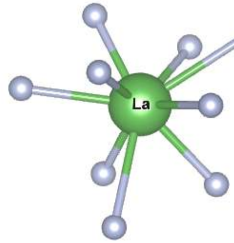
>2000 members on the forum
800 kLines of F90
about 50 contributors to ABINITv8

Ab Initio at work: Ce-doped lanthanum silicon nitrides

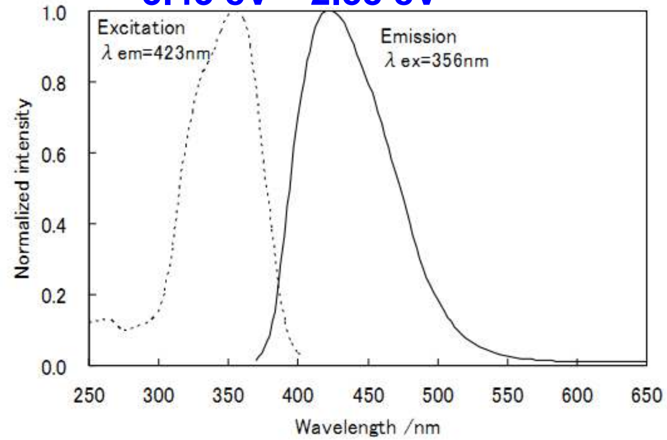
Ce^{3+} ion in $LaSi_3N_5$ and $La_3Si_6N_{11}$ (LSN)

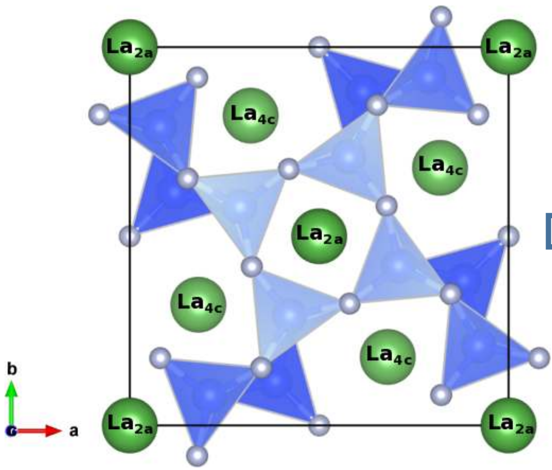


$LaSi_3N_5$:Ce



3.43 eV 2.58 eV

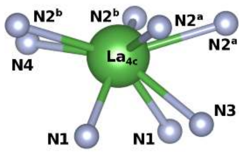




$La_3Si_6N_{11}$:Ce_{2a}

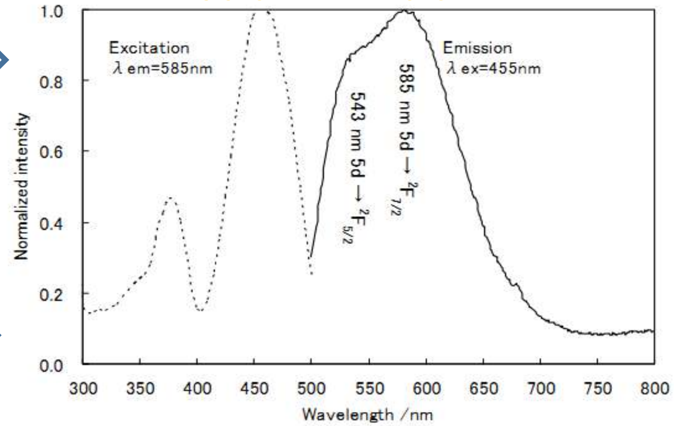
?

$La_3Si_6N_{11}$:Ce_{4c}



?

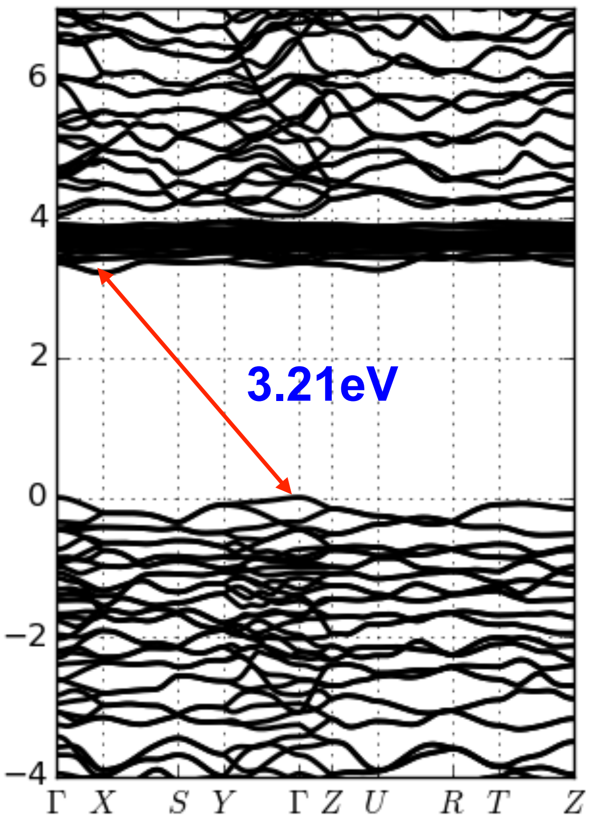
2.95 eV 2.25 eV



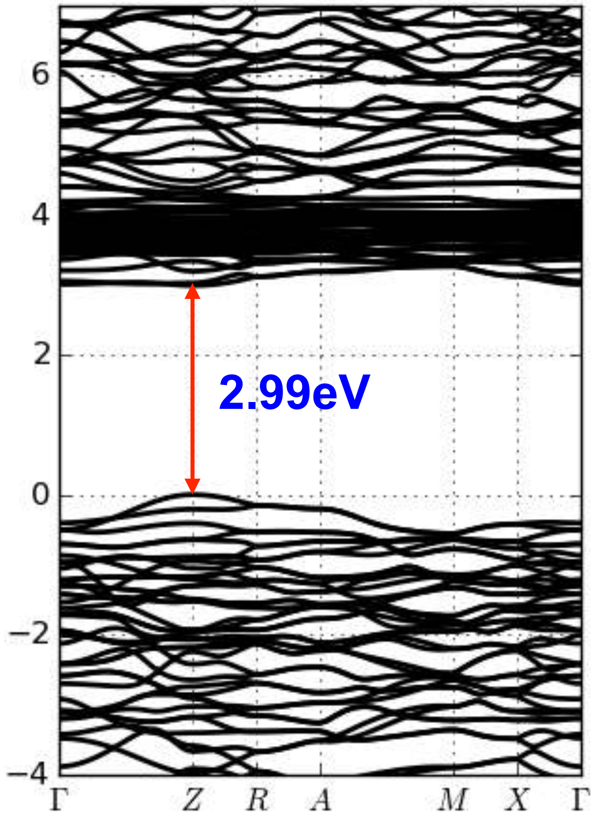
- The reason for the different emission color ?
- The luminescent center in the $La_3Si_6N_{11}$:Ce ?

Suehiro et al, APL, 95, 051903(2009)
Kijma et al, ECS Trans. 25, 247 (2009)

LSN DFT electronic structure



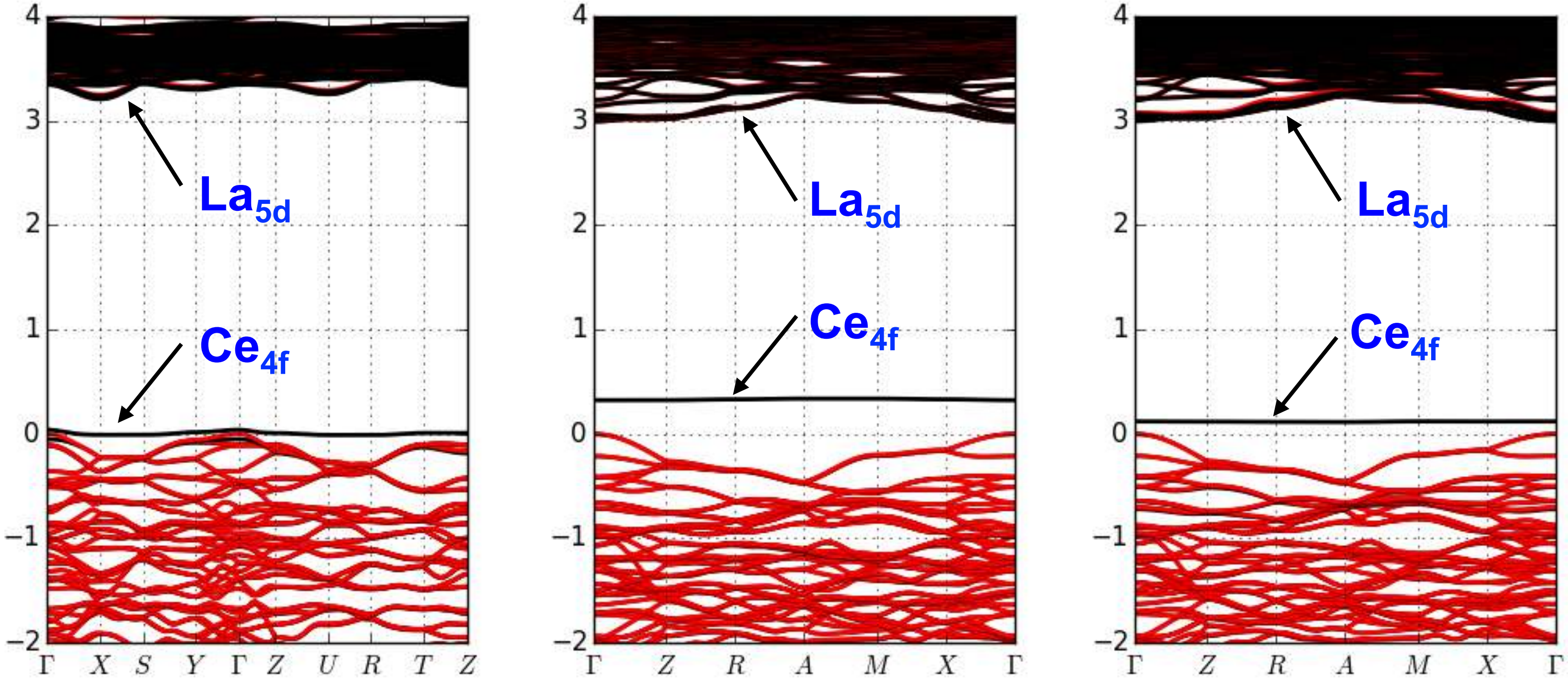
$LaSi_3N_5$



$La_3Si_6N_{11}$

- Ab-initio simulation: Density functional theory (DFT), GGA level

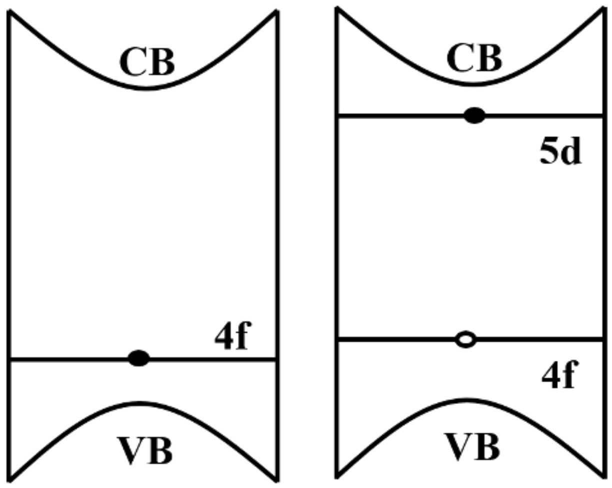
Ce-doped LSN : DFT electronic structure



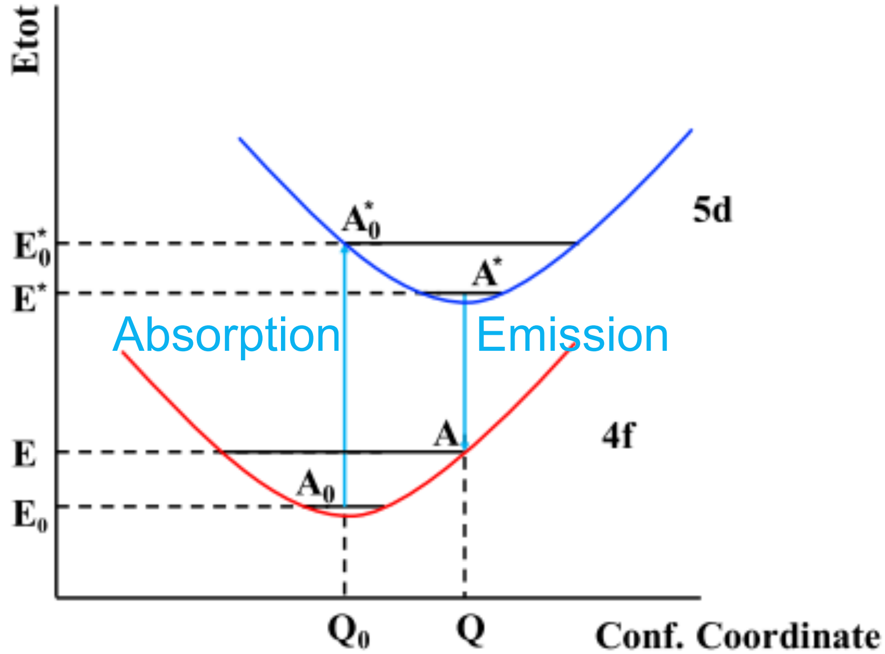
$LaSi_3N_5$:Ce　　$La_3Si_6N_{11}$:Ce_{2a}　　$La_3Si_6N_{11}$:Ce_{4c}

- The description of Ce_{4f} state relies on the DFT+U method, U = 4.6eV
- Ce_{5d} state not located inside band gap in ground state calculation
  (DOES **NOT** correspond to luminescent excited state of LSN:Ce)

ΔSCF method



Ground state　　ΔSCF



Configuration diagram

- ΔSCF method: mimic the interaction between electrons and a 4f-hole. Comparison of total energies of ground and excited states.
- Calculate transition energy based on configuration coordination diagram (Seitz 1938, Mott 1938, Gurney 1939 …).

For scintillator absorption see also : Chaudhry, Canning et al, PRB 83, 125155 (2011), JAP 109, 083708 (2011), PRB 89, 155105 (2014)

Ce-doped LSN : excited state electronic structure

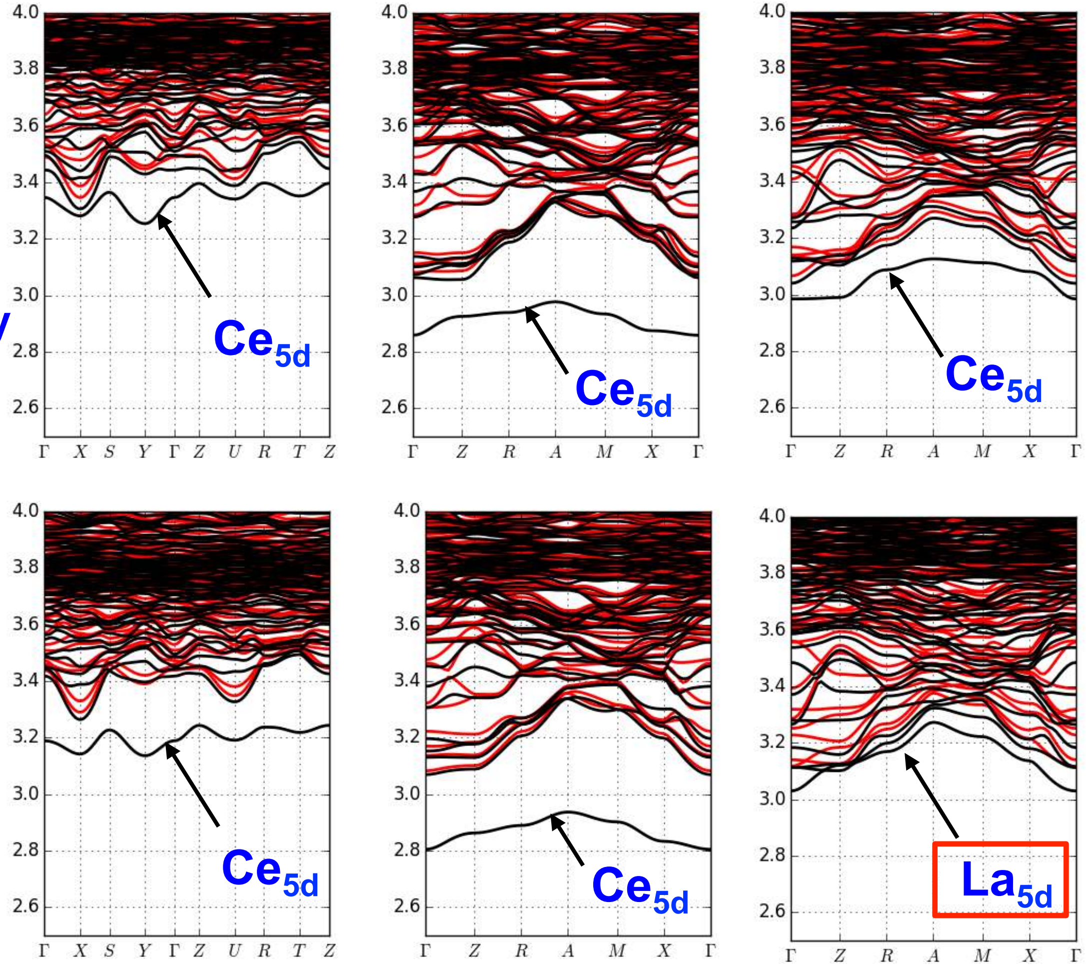
$LaSi_3N_5$:Ce | **$La_3Si_6N_{11}$:Ce_{2a}** | **$La_3Si_6N_{11}$:Ce_{4c}**

A_0^* case

Excited-state Absorption geometry

A^* case

Excited-state Emission geometry



(non-Luminescent)

- Core-hole interaction and anti-bonding character affect position of Ce_{5d} state

ΔSCF Energies in ground- and excited-states

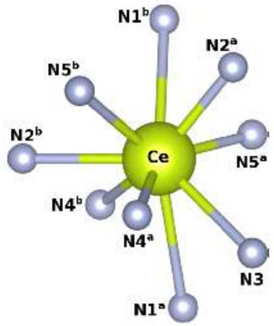
Case	$LaSi_3N_5$:Ce	$La_3Si_6N_{11}$:Ce_{2a}	$La_3Si_6N_{11}$:Ce_{4c}
A_0	-20774.76eV	-25363.89eV	-25363.98eV
A_0*	-20771.26eV	-25361.10eV	-25360.70eV
A	-20774.53eV	-25363.68eV	-25363.52eV
A*	-20771.42eV	-25361.28eV	-25360.92eV
$\Delta E_{abs}(A_0^*-A_0)$	3.50eV	2.79eV	3.28eV
ΔE_{abs}(Exp.)	3.43eV	2.58eV	--------
$\Delta E_{em}(A^*-A)$	3.12eV	2.40eV	2.60eV
ΔE_{em}(Exp.)	2.95eV	2.25eV	--------
ΔS(Cal.)	$3080cm^{-1}$	$3160cm^{-1}$	$5456cm^{-1}$
ΔS(Exp.)	$3815cm^{-1}$	$2717cm^{-1}$	--------

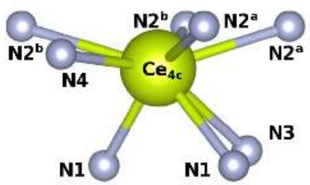
$1000cm^{-1}$=0.124eV Y. Jia *et al*, PRB, 93, 15111 (2016)

- Accurate absorption and emission energy, within 0.2eV error.
- Stokes shift value is provided within 20% difference.
- Luminescent center in $La_3Si_6N_{11}$:Ce is determined to be Ce_{2a} site

Ce environment and Dorenbos model parameters

		LaSi$_3$N$_5$:Ce	9 NN
Bond	Ground	Excited	Geometry
Ce-N 1^a	3.151	3.178	
Ce-N 1^b	3.137	**3.324**	
Ce-N 2^a	2.430	2.380	
Ce-N 2^b	2.717	**2.601**	
Ce-N3	2.874	2.955	
Ce-N 4^a	2.553	2.416	
Ce-N 4^b	2.898	2.835	
Ce-N 5^a	2.690	2.792	
Ce-N 5^b	2.850	**2.712**	
		La$_3$Si$_6$N$_{11}$:Ce$_{2a}$	8 NN
Ce-N1 (x4)	2.657	2.645	
Ce-N2 (x4)	2.638	**2.555**	
		La$_3$Si$_6$N$_{11}$:Ce$_{4c}$	8 NN
Ce-N1(x2)	2.512	2.389	
Ce-N2^a (x2)	2.670	2.596	
Ce-N2^b (x2)	2.901	2.895	
Ce-N3	2.802	2.718	
Ce-N4	2.641	**2.472**	





–	LaSi$_3$N$_5$:Ce	La$_3$Si$_6$N$_{11}$:Ce$_{2a}$	La$_3$Si$_6$N$_{11}$:Ce$_{4c}$
χ_{av}	1.74	1.68	1.68
α_{sp}^N	7.07	7.52	7.52
ε_c, GS	21380 cm^{-1}	25166 cm^{-1}	23671 cm^{-1}
ε_c, EX	23950 cm^{-1}	28242 cm^{-1}	–
β	5.67×10^8	1.20×10^9	1.20×10^9
R$_{av}$, GS	281 pm	265 pm	270 pm
R$_{av}$, EX	280 pm	260 pm	–
ε_{cfs}, GS	7181 cm^{-1}	17088 cm^{-1}	16461 cm^{-1}
ε_{cfs}, EX	7232 cm^{-1}	17751 cm^{-1}	–

$$D(A) = \varepsilon_c(A) + \frac{\varepsilon_{cfs}(A)}{r(A)} - 1890cm^{-1}$$

$$\varepsilon_c(A) = 1.44 \times 10^{17} \Sigma_{i=1}^{N} \frac{\alpha_{sp}^i}{R_i^6}.$$

$$\alpha_{sp} = \alpha_0 + \frac{b}{\chi^2}$$

$$\varepsilon_{cfs} = \frac{\beta}{R_{av}^2}$$

Depend on type of coordination incl. # NN

$$E(A) = 49340cm^{-1} - D(A)$$

Scaling up : results for 28 Ce- and Eu-doped hosts

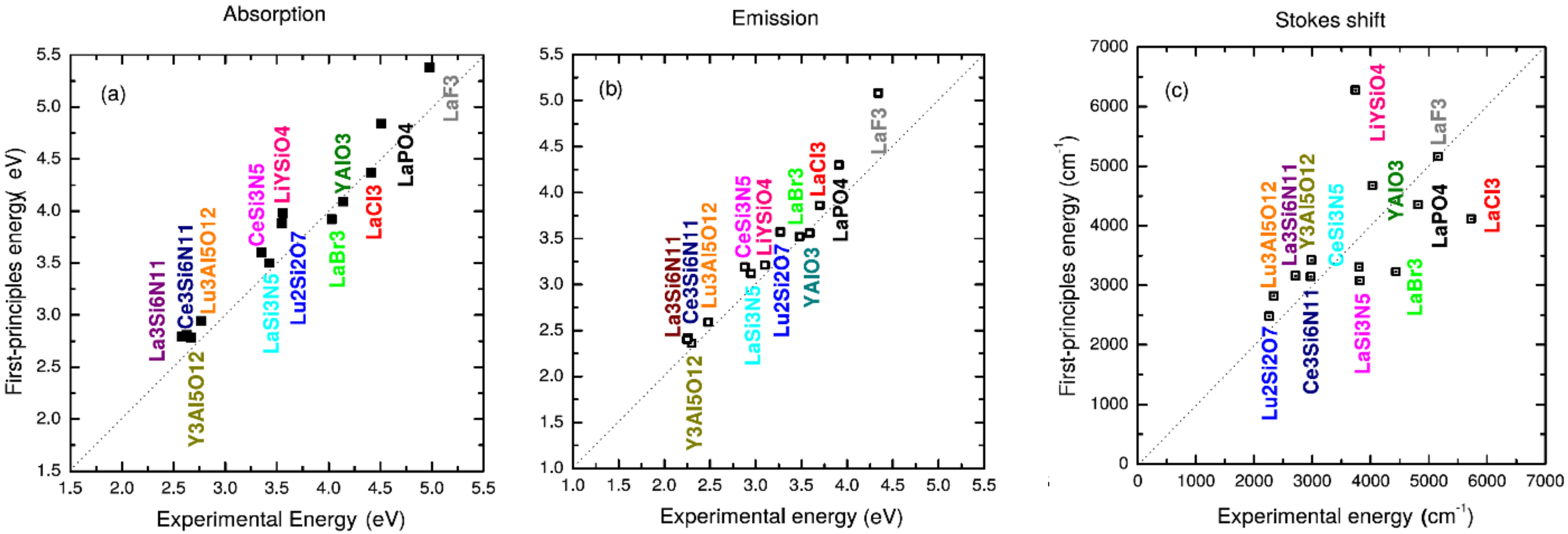
Thirteen Ce-doped hosts covering 2-5 eV range

	Compounds	Calculation (this work)			Experiment		
		Abs (eV)	Em (eV)	ΔS (cm^{-1})	Abs (eV)	Em (eV)	ΔS (cm^{-1})
LSN →	$La_3Si_6N_{11}$:Ce	2.79	2.40	3160	2.58	2.25	2710
	$Ce_3Si_6N_{11}$	2.81	2.42	3146	2.63	2.26	2974
YAG →	$Y_3Al_5O_{12}$:Ce	2.78	2.36	3424	2.67	2.30	2984
	$Lu_3Al_5O_{12}$:Ce	2.94	2.59	2823	2.77	2.48	2339
	$CeSi_3N_5$	3.60	3.19	3307	3.35	2.88	3815
LSN →	$LaSi_3N_5$:Ce	3.50	3.12	3080	3.43	2.95	3815
	$LiYSiO_4$:Ce	4.02	3.33	5575	3.54	3.10	3740
	$Lu_2Si_2O_7$:Ce	3.88	3.57	2480	3.55	3.27	2258
	$LaBr_3$:Ce	3.92	3.52	3226	4.03	3.48	4439
	$YAlO_3$:Ce	4.14	3.56	4678	4.09	3.59	4033
	$LaCl_3$:Ce	4.37	3.86	4113	4.41	3.70	5726
	$LaPO_4$:Ce	4.84	4.30	4355	4.51	3.91	4818
	LaF_3:Ce	5.38	**4.74**	5162	4.98	4.34	5162

Jia, Poncé, Miglio, Mikami & Gonze, Adv. Opt. Materials, 5, 1600997(2017)

Wide applicability of the first-principles methodology

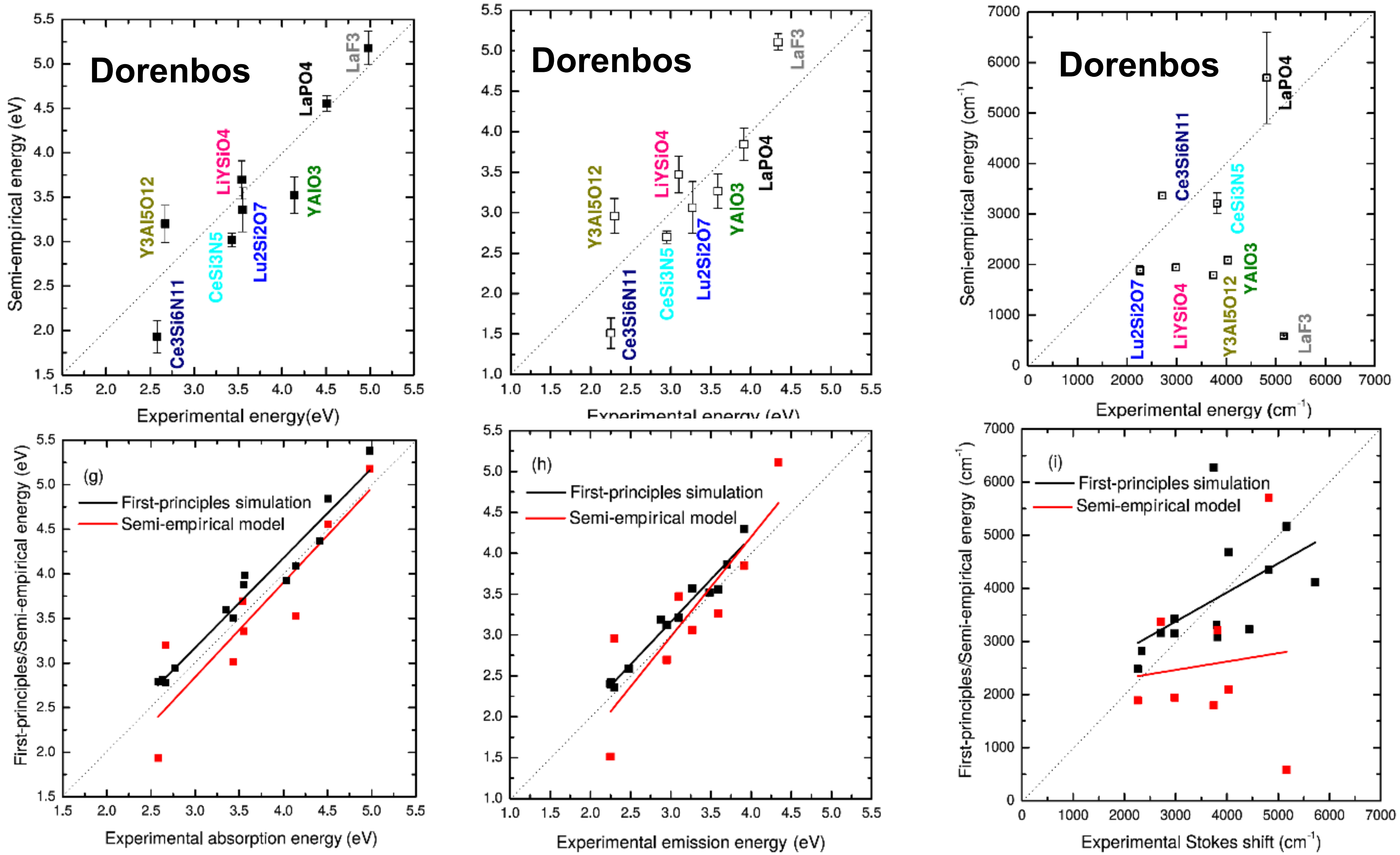
First-principles



- First-principles absorption and emission energy are within 0.3 eV of experimental data, with two exceptions at 0.4 eV and 0.5 eV
- First-principles Stokes shifts are within 30%, except two values at 50%

Jia, Poncé, Miglio, Mikami & Gonze, Adv. Opt. Materials, 5, 1600997(2017)

Using first-principles geometrical parameters in Dorenbos model : larger dispersion



Jia, Poncé, Miglio, Mikami & Gonze, Adv. Opt. Materials 1600997(2017)

Statistical analysis

ME Mean Error
MAE Mean Absolute Error
MRE Mean Relative Error
MARE Mean Absolute Relative Error

	First-principles			Semi-empirical		
	Absorption	Emission	Stokes shift	Absorption	Emission	Stokes shift
ME	0.175 eV	0.205 eV	33.5 cm^{-1}	-0.118 eV	0.027 eV	**-1118 cm^{-1}**
MAE	0.205 eV	0.210 eV	**728 cm^{-1}**	0.350 eV	0.423 eV	**1502 cm^{-1}**
MRE (%)	5.100	6.280	4.17	3.540	-0.01	**-26.7**
MARE (%)	5.850	6.410	**19.1**	**10.8**	**14.6**	**37.3**
Slope	1.050	1.040	0.547	1.06	**1.22**	**0.158**
Intercept	0.156	0.038	1734	-0.034	-0.682	1989
R-Square (%)	95.10	96.10	25.00	78.8	72.3	**-15.4**

First-principle methodology clearly better than semi-empirical Dorenbos approach
Still, the latter has the correct trends, and single out important factors

Jia, Poncé, Miglio, Mikami & Gonze, Adv. Opt. Materials, 5, 1600997(2017)

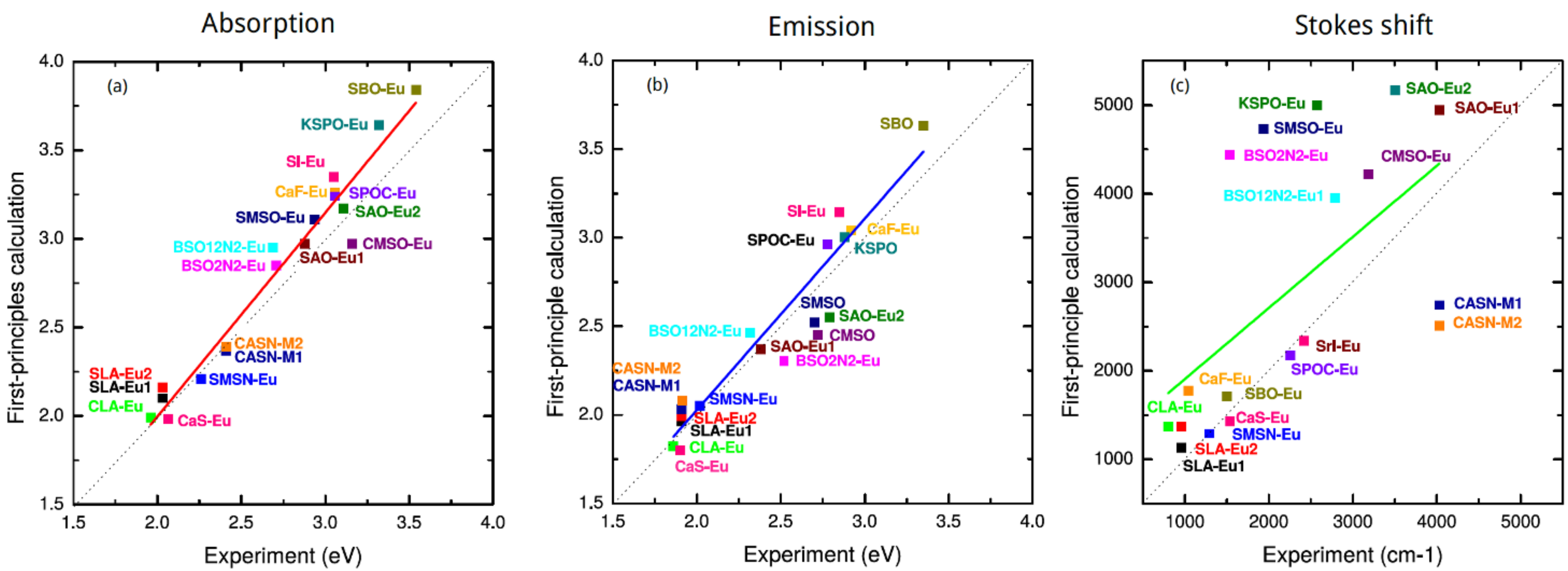
Fifteen Eu-doped hosts covering 2-3.5 eV range

Compound	Calculation			Experiment		
	Abs	Em	ΔS	Abs	Em	ΔS
$Sr[LiAl_3N_4]$:Eu1	2.10	1.96	1129	2.03	1.91	956
$Sr[LiAl_3N_4]$:Eu2	2.16	1.99	1371	2.03	1.91	956
$Ca[LiAl_3N_4]$:Eu	1.99	1.82	1371	1.96	1.86	800
$Sr[Mg_3SiN_4]$:Eu	2.21	2.05	1290	2.26	2.02	1935
$Ba_3Si_6O_{12}N_2$:Eu	2.95	2.46	3952	2.69	2.32	2790
$BaSi_2O_2N_2$:Eu	2.85	2.30	**4436**	2.71	2.52	1532
$CaAlSiN_3$:Eu,M-I	2.37	2.03	2742	2.41	1.91	4032
$CaAlSiN_3$:Eu,M-II	2.39	2.08	2508	2.41	1.91	4032
$SrAl_2O_4$:Eu1	2.97	2.37	4839	2.88	2.38	4033
$SrAl_2O_4$:Eu2	3.17	2.55	**4996**	3.11	2.79	2581
$Sr_5(PO_4)_3Cl$:Eu	3.24	2.96	2258	3.06	2.78	2178
SrI_2:Eu	3.35	3.14	2339	3.05	2.85	2420
CaF_2:Eu	3.26	3.04	1774	3.06	2.92	1047
CaS:Eu	1.97	1.80	1399	2.07	1.90	1466
$SrBO_4$:Eu	3.84	3.63	1710	3.54	3.35	1502
$Sr_2MgSi_2O_7$:Eu	3.11	2.52	**4726**	2.94	2.70	1936
$CaMgSi_2O_6$:Eu	2.97	2.45	4218	3.16	2.72	3188
$KSrPO_4$:Eu	3.61	3.00	**4920**	3.32	2.88	3500

	First-principles		
	Absorption	Emission	Stokes shift
ME	0.104 eV	0.058 eV	428 cm^{-1}
MAE	0.154 eV	0.159 eV	**819** cm^{-1}
MRE (%)	3.55	2.27	33.7
MARE (%)	5.50	6.36	**44.2**
Slope	1.156	1.081	0.704
Intercept	-0.310	-0.135	1117
R-Square (%)	94.4	89.1	25.5

Jia, Poncé, Miglio, Mikami & Gonze, PRB 96, 125132 (2017).

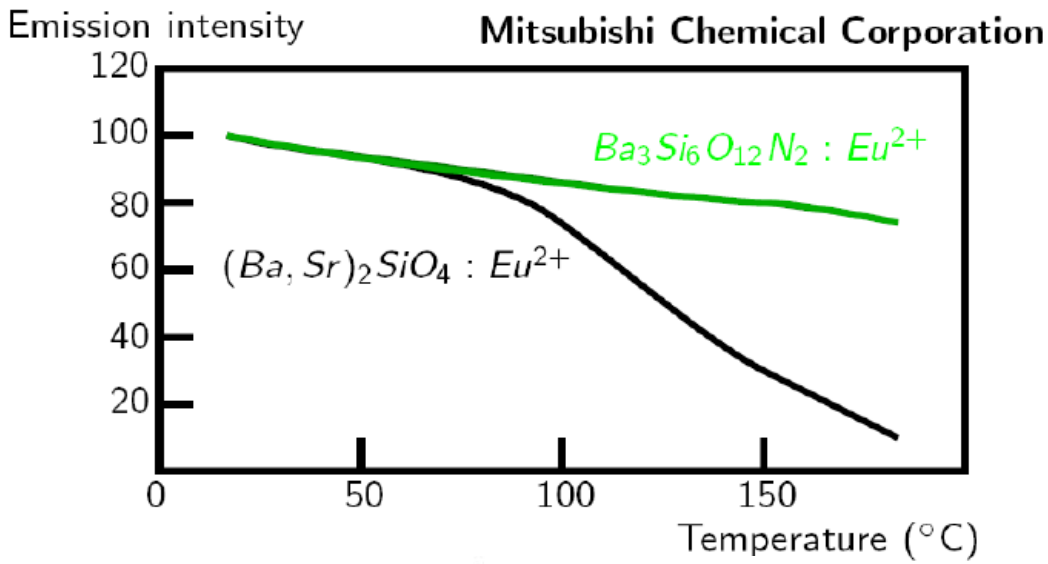
Fifteen Eu-doped hosts covering 2-3.5 eV range

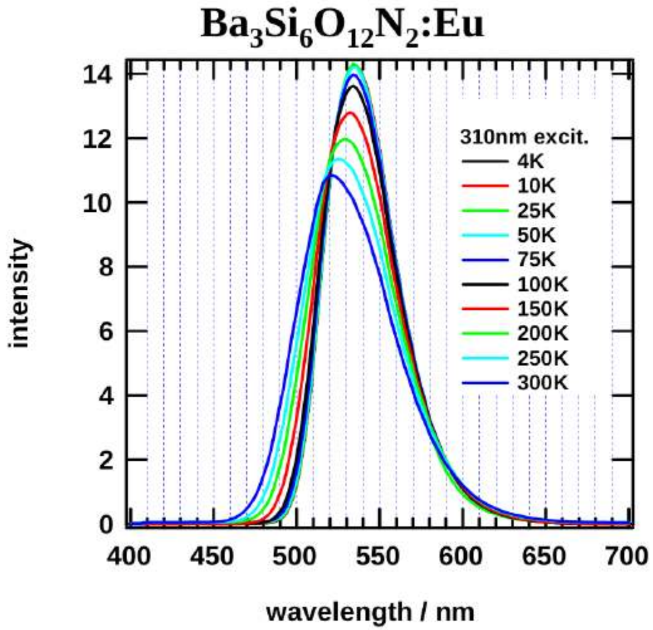


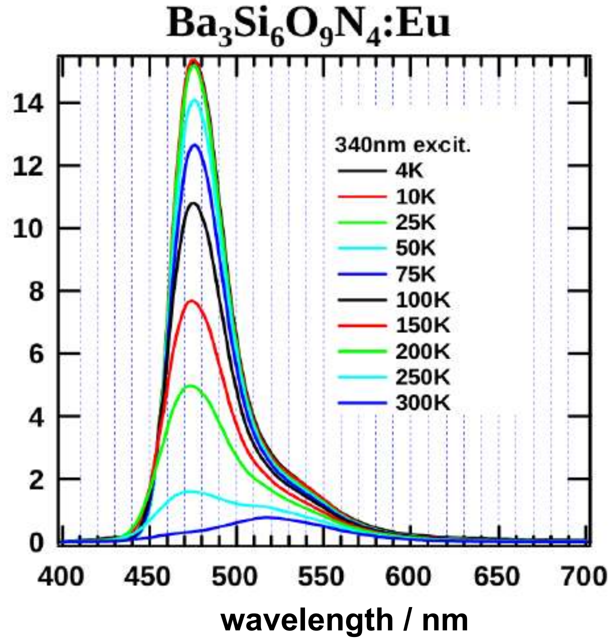
Jia, Poncé, Miglio, Mikami & Gonze, PRB 96, 125132 (2017).

Thermal quenching ?
Emission width ?
The 1-D model and beyond

Thermal quenching

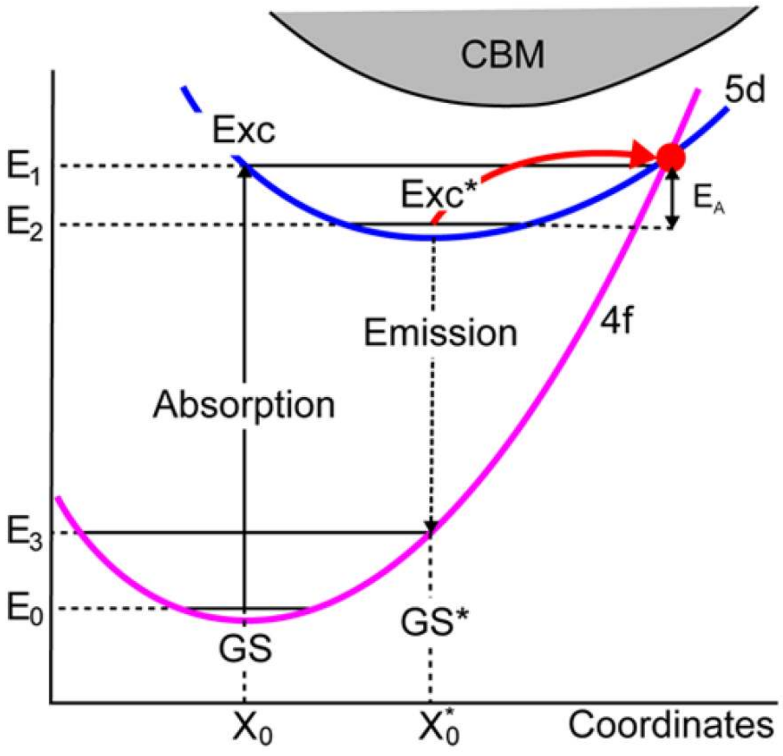




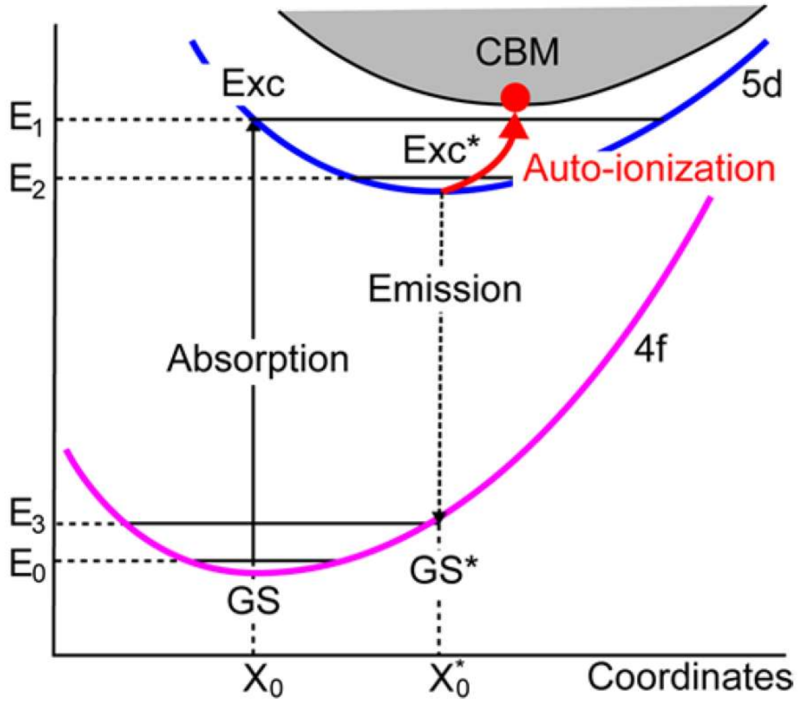


See e.g. C. Braun … W. Schnick, Chem. Eur. J. 16, 9646 (2010)

Models for thermal quenching



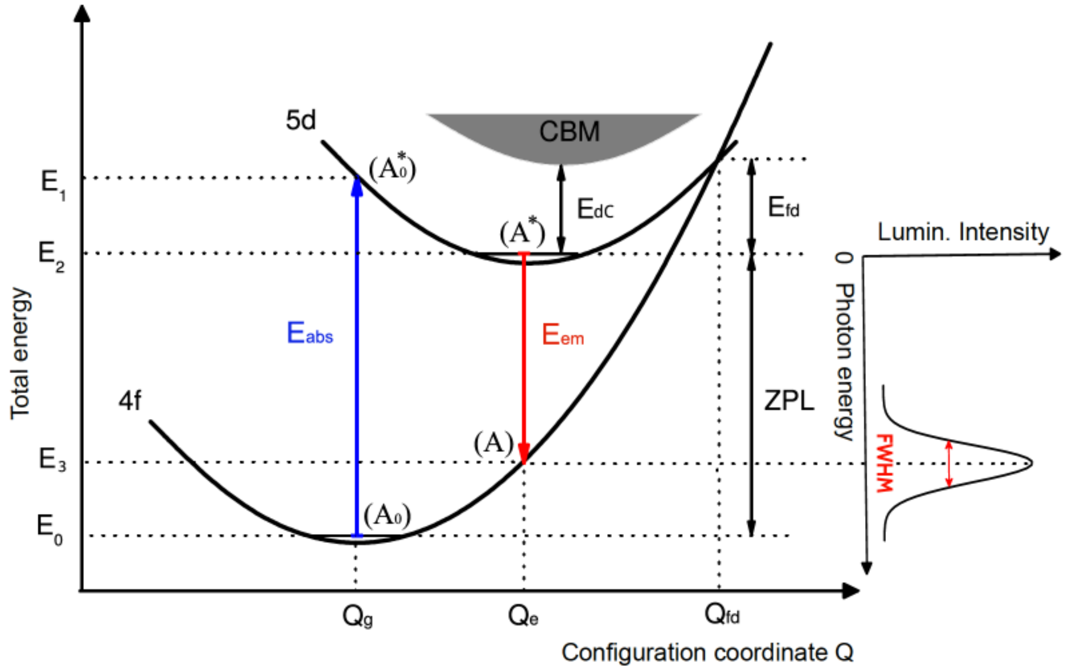
(a) 4f-5d crossing model

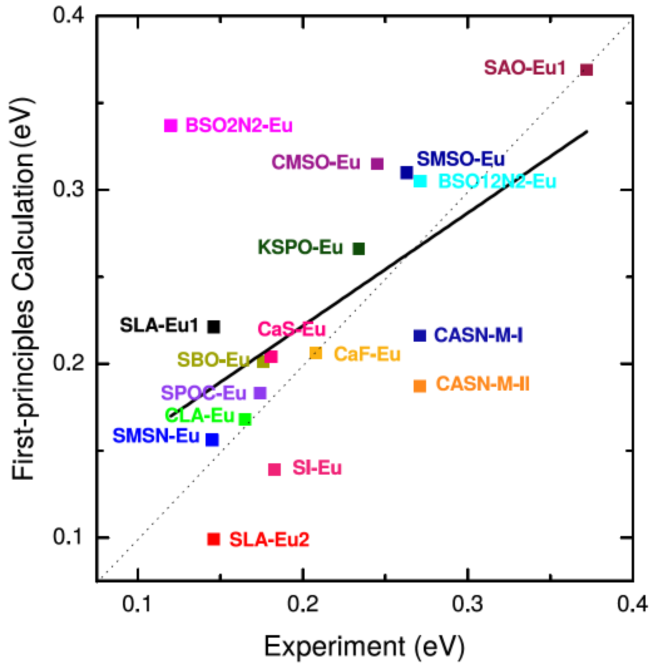


(b) Dorenbos auto-ionization model

- The 4f-5d energy barrier (E_A) can be estimated in a 1-D picture + parabolic approximation, with only the usual 4 total energy calculations
- For the fifteen Eu-doped hosts, the energy barrier is estimated to be 1.9 eV or (much) larger. In favor of auto-ionization !

Emission : Full width at half maximum





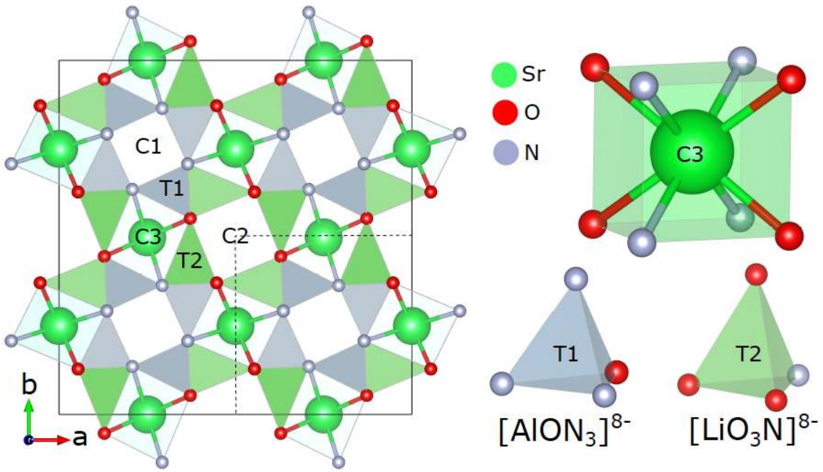
	First-principles calculation			
	Absorption	Emission	Stokes shift	FWHM
ME	0.104	0.058	428	0.018
MAE	0.154	0.159	819	0.046
MRE (%)	3.55	2.27	33.70	13.94
MARE (%)	5.50	6.36	44.2	26.81
Slope	1.156	1.081	0.704	0.650
Intercept	-0.310	-0.135	1117	0.092
R-Square (%)	94.4	89.1	25.5	26.7

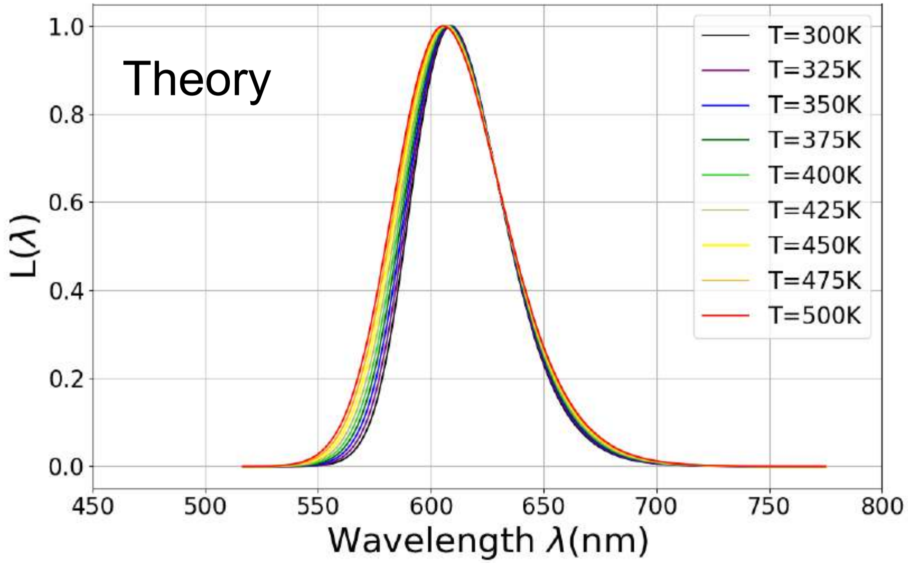
Jia, Poncé, Miglio, Mikami & Gonze, PRB 96, 125132 (2017).

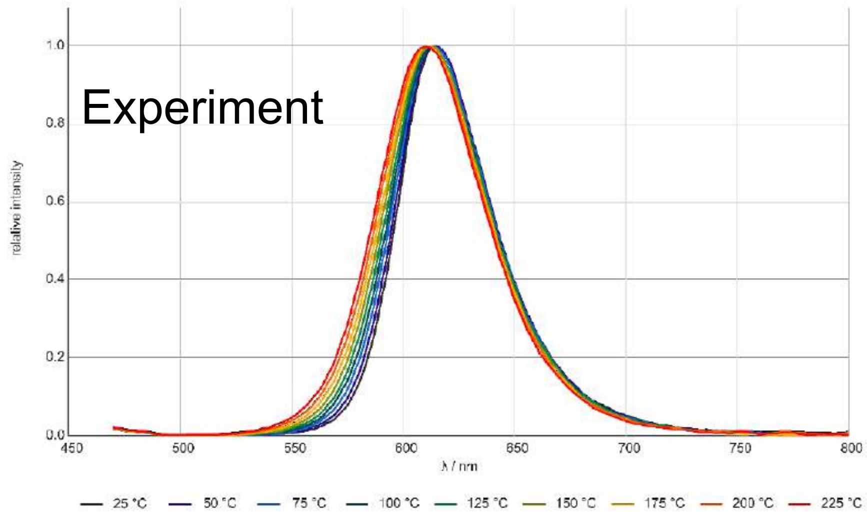
Emission : shape/shift of the spectrum

Recently discovered
$Sr[Li_2Al_2O_2N_2]:Eu^{2+}$ phosphor

G.J. Hoerder et al, *Nature Comm. 10, 1824 (2019)*

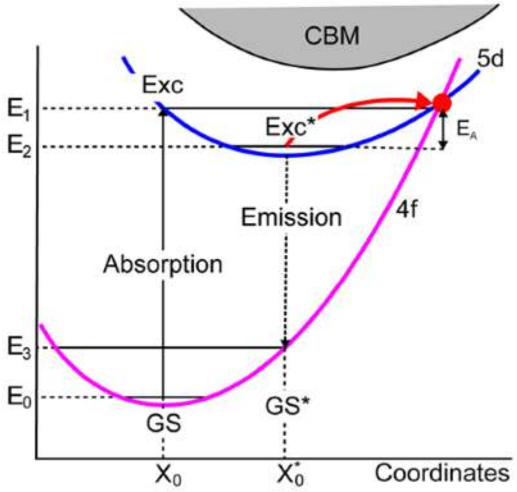






J. Bouquiaux, Y. Jia, S. Poncé, A. Miglio, M. Mikami & X. Gonze, *arXiv:cond-mat.mtrl-sci 2010:00423 (2020) and in preparation*

Beyond the 1D model: 4f-5d crossing

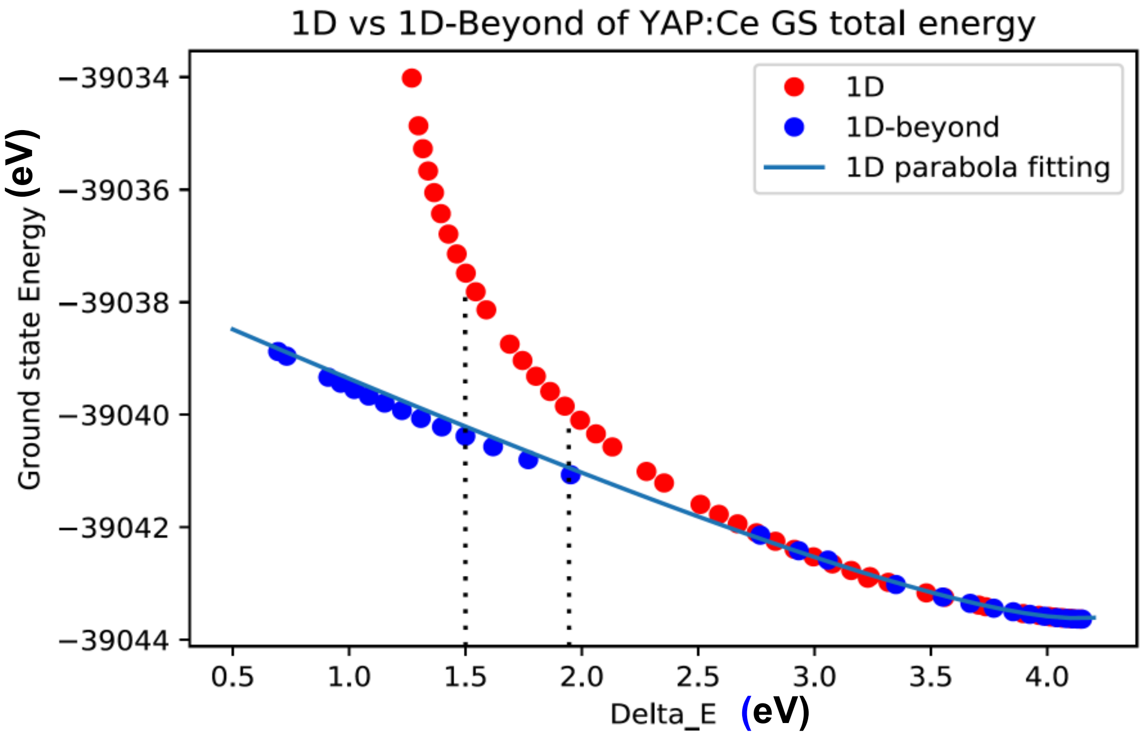


(a) 4f-5d crossing model

- More general statement of problem: in full coordinate space, find lowest E_A for a given ΔE(5d-4f) (that might be zero)
- Adressed by Lagrange multiplier technique: geometry optimization on linked 4f and 5d systems

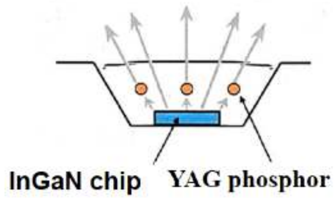
- Example for $YAlO_3$:Ce
- Energy barrier is indeed lowered w.r.t. 1D model
- But not so much w.r.t parabolic approximation

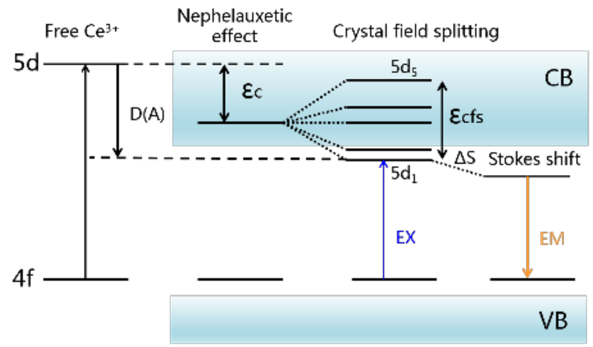
Jia, Poncé, Miglio, Mikami & Gonze, *Phys. Rev. B* 100, 155109 (2019)



Wrap-up

The most efficient white LEDs are phosphor-based : downconversion of blue light

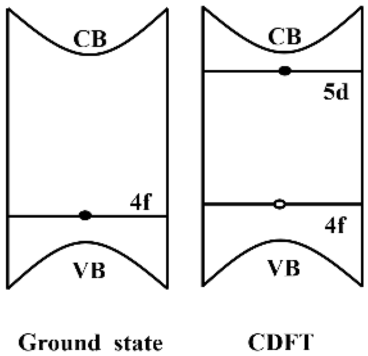


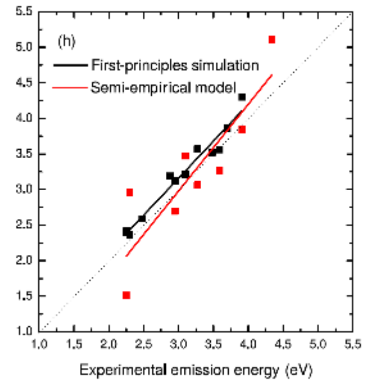


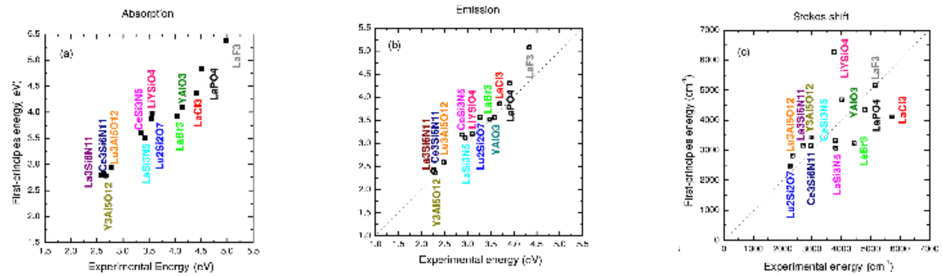
Need to optimize : Emission spectrum ; Excitation spectrum ; Quantum efficiency ; Optical characteristics at elevated temperature ; …

Ce^{3+} and Eu^{2+} - doped inorganic hosts : tunable 4f – 5d transition

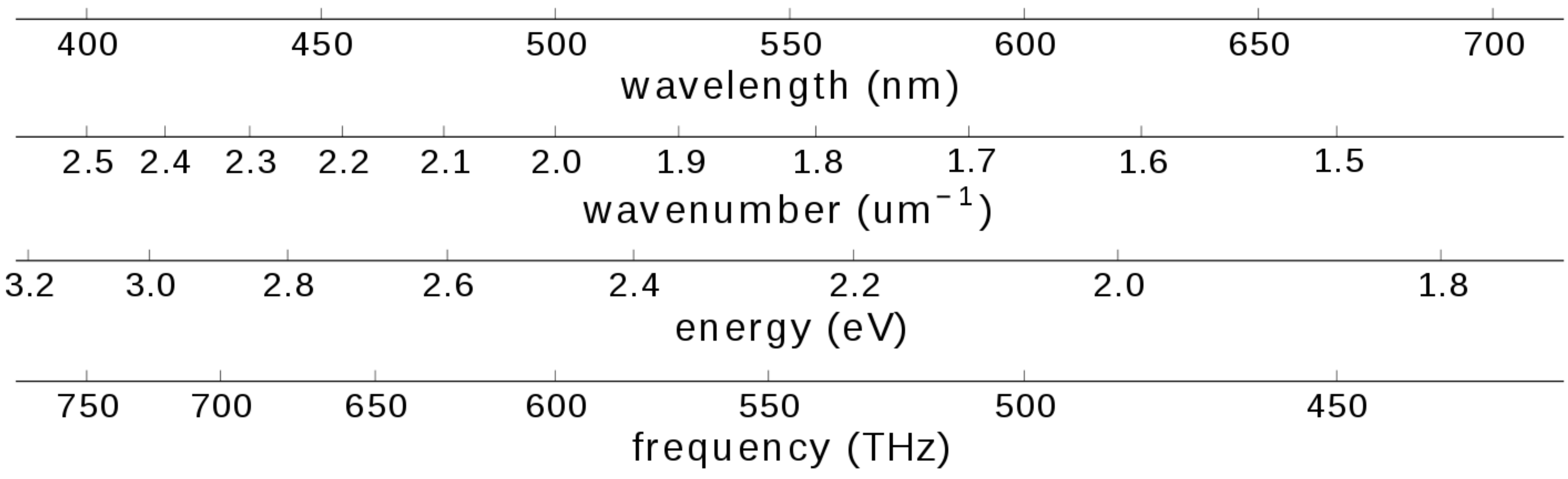
- First-principle methodology
- Absorption, emission & Stokes shift
- Study of 13 Ce-doped hosts and 18 Eu-doped hosts, to validate the methodology.
- Outperform the semi-empirical methodology (useful to get physical insights !)
- Thermal quenching & width







Units for the visible spectrum



Detailed information of semi-empirical fitting

Compounds	State	χ_{av}	α_{sp}^{i}	ε_c	β	R_{av}	ε_{cfs}	D(A) r=1.7	D(A) r=2.4	D(A) average
YAG:Ce	GS	1.425	2.694	13671cm^{-1}	1.2×10^9	247.5pm	19614cm^{-1}	25209cm^{-1}	21844cm^{-1}	23526cm^{-1}
	EX	1.425	2.694	15253cm^{-1}	1.2×10^9	243.1pm	20331cm^{-1}	27212cm^{-1}	23724cm^{-1}	25468cm^{-1}
LuAG:Ce	GS	1.483	2.514	17612cm^{-1}	1.2×10^9	234.6pm	21803cm^{-1}	30437cm^{-1}	26697cm^{-1}	28567cm^{-1}
	EX	1.483	2.514	14446cm^{-1}	1.2×10^9	242.3pm	20440cm^{-1}	26470cm^{-1}	22963cm^{-1}	24717cm^{-1}
$LaPO_4$:Ce	GS	1.725	1.934	8403cm^{-1}	5.67×10^8	260.3pm	8368cm^{-1}	13325cm^{-1}	11890cm^{-1}	12608cm^{-1}
	EX	1.725	1.934	8822cm^{-1}	1.2×10^9	252.3pm	18875cm^{-1}	19925cm^{-1}	16687cm^{-1}	18306cm^{-1}
$Lu_2Si_2O_7$:Ce	GS	1.543	2.346	10553cm^{-1}	1.35×10^9	240.7pm	23301cm^{-1}	24259cm^{-1}	20262cm^{-1}	22261cm^{-1}
	EX	1.543	2.346	11938cm^{-1}	1.35×10^9	235.7pm	24300cm^{-1}	26232cm^{-1}	22063cm^{-1}	24148cm^{-1}
$LaSi_3N_5$:Ce	GS	1.74	7.07	21380cm^{-1}	5.67×10^8	281pm	7181cm^{-1}	25604cm^{-1}	24372cm^{-1}	24988cm^{-1}
	EX	1.74	7.07	23950cm^{-1}	5.67×10^8	280pm	7232cm^{-1}	28204cm^{-1}	26963cm^{-1}	27584cm^{-1}
$La_3Si_6N_{11}$:Ce	GS	1.68	7.52	25166cm^{-1}	1.2×10^9	265pm	17088cm^{-1}	35218cm^{-1}	32286cm^{-1}	33752cm^{-1}
	EX	1.68	7.52	28242cm^{-1}	1.20×10^9	260pm	17751cm^{-1}	38683cm^{-1}	35638cm^{-1}	37161cm^{-1}
$CeSi_3N_5$	GS	1.74	7.07	21445cm^{-1}	5.67×10^8	280.8pm	7191cm^{-1}	25675cm^{-1}	24441cm^{-1}	25058cm^{-1}
	EX	1.74	7.07	23885cm$_{-1}$	5.67×10^8	280.7pm	7196cm$_{-1}$	28118cm^{-1}	26883cm^{-1}	27501cm^{-1}
$Ce_3Si_6N_{11}$	GS	1.69	7.46	25154cm^{-1}	1.2×10^9	264.4pm	17166cm^{-1}	35222cm^{-1}	32306cm^{-1}	33779cm^{-1}
	EX	1.69	7.46	28198cm^{-1}	1.20×10^9	259.6pm	17806cm^{-1}	38672cm^{-1}	35617cm^{-1}	37145cm^{-1}

The bright present and future of blue and white LEDs

- blu-ray technology (high-density DVDs, laser printers)
- white lighting (public, home, industry, greenhouse, transportation...)
- dominant technology in back-illuminated liquid crystal displays (mobile phones, tablets, laptops, computer monitors, TV screens ...)

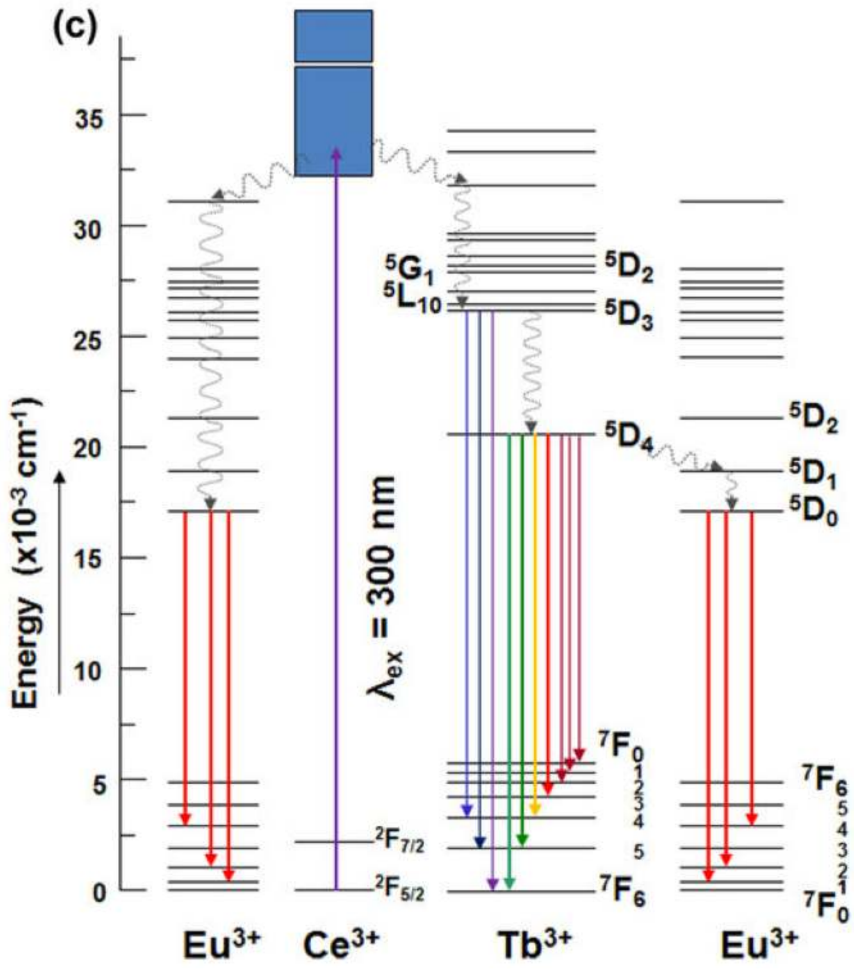
Future

- UV for water purification
- Optical RGB white-LED wireless transmission (> 3 Gbits/sec)

Blu-ray Disc™

UCLouvain Skoltech RSF Russian Science Foundation Abinit ETSF

Excitation Spectra of Ce3+ and Eu3+

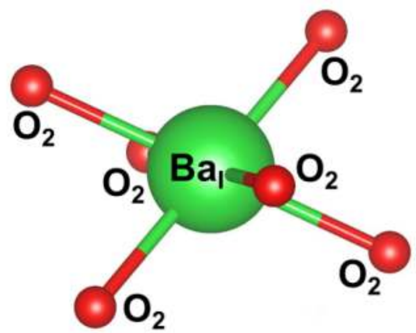


Important effect of spin-orbit coupling.

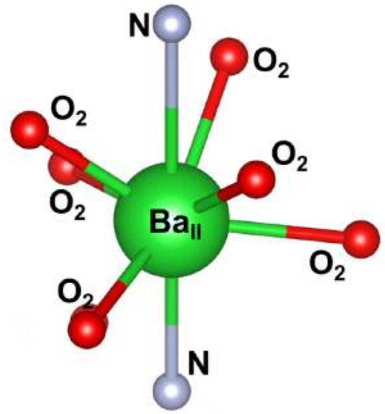
Kim et al, Sci. Reports 5, 7866 (2015).

Geometry relaxation : $Ba_3Si_6O_{12}N_2$

	undoped[b]	ground state		excited state	
		Eu	diff %	Eu	diff %
X_I-O_2 (6×)	2.760	2.532	−8.3	2.388	−13.5
$X_{II}-O_2$ (3×)	2.959	2.869	−3.0	2.798	−5.4
$X_{II}-O_2$ (3×)	2.812	2.528	−10.1	2.352	−16.4
$X_{II}-N$ (1×)	3.054	2.878	−5.8	2.763	−9.5
$X_{II}-N$ (1×)	3.499	3.464	−1.0	3.578	2.3



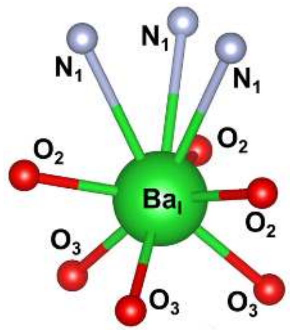
(a) Ba_I in $Ba_3Si_6O_{12}N_2$



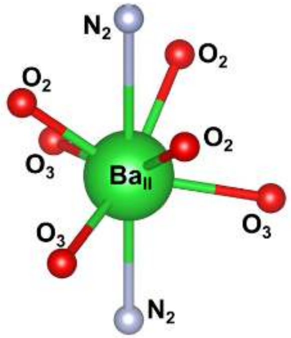
(b) Ba_{II} in $Ba_3Si_6O_{12}N_2$

Geometry relaxation : $Ba_3Si_6O_9N_4$

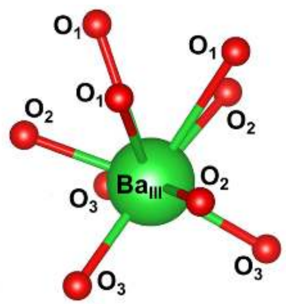
	undoped[b]	ground state		excited state	
		Eu	diff %	Eu	diff %
X_I-O_2 (3×)	2.714	2.561	−5.6	2.414	−11.0
X_I-O_3 (3×)	2.823	2.582	−8.5	2.489	−11.8
X_I-N_1 (3×)	3.498	3.729	6.6	3.768	7.7
$X_{II}-O_2$ (3×)	2.703	2.437	−9.8	2.343	−13.3
$X_{II}-O_3$ (3×)	2.860	2.758	−3.6	2.629	−8.1
$X_{II}-N_2$ (1×)	3.284	3.183	−3.1	3.059	−6.8
$X_{II}-N_2$ (1×)	3.579	3.469	−3.1	3.593	0.4
$X_{III}-O_2$ (3×)	2.730	2.535	−7.2	2.421	−11.3
$X_{III}-O_3$ (3×)	2.731	2.553	−6.5	2.450	−10.3
$X_{III}-O_1$ (3×)	3.375	3.579	6.0	3.388	0.4



(c) Ba_I in $Ba_3Si_6O_9N_4$

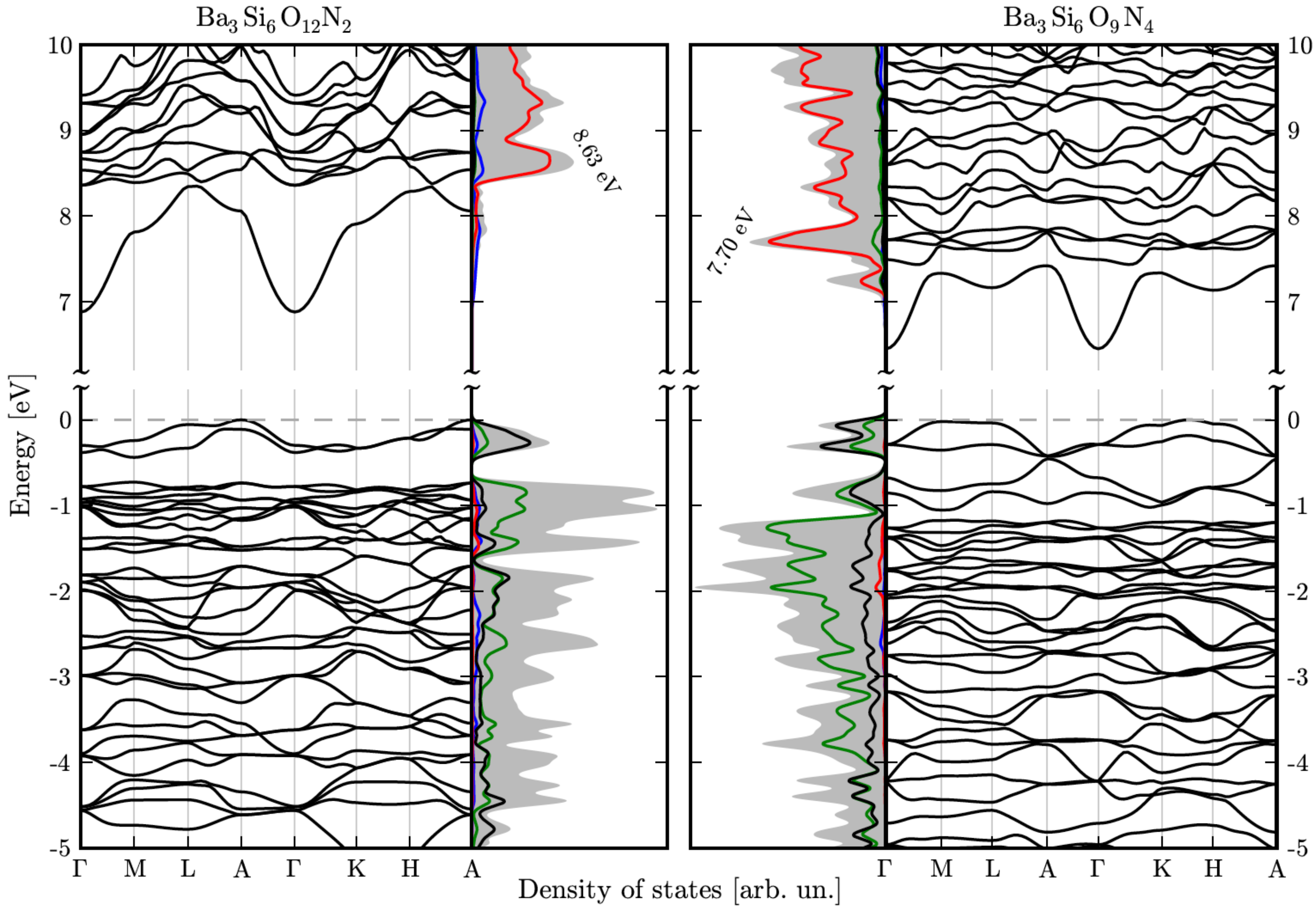


(d) Ba_{II} in $Ba_3Si_6O_9N_4$

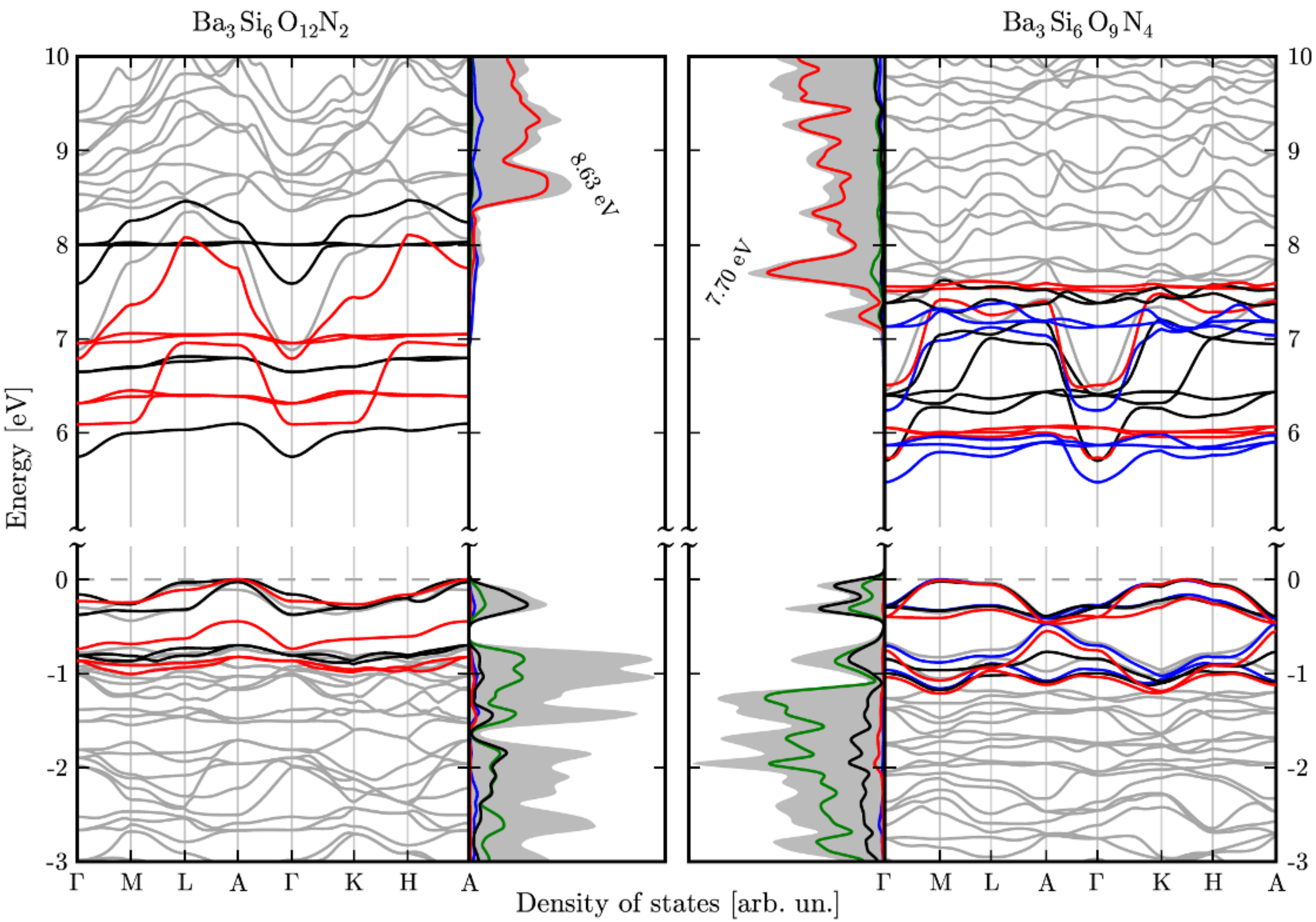


(e) Ba_{III} in $Ba_3Si_6O_9N_4$

Host band structure comparison (GW)



Eu-doped band structure (excited state - GW)

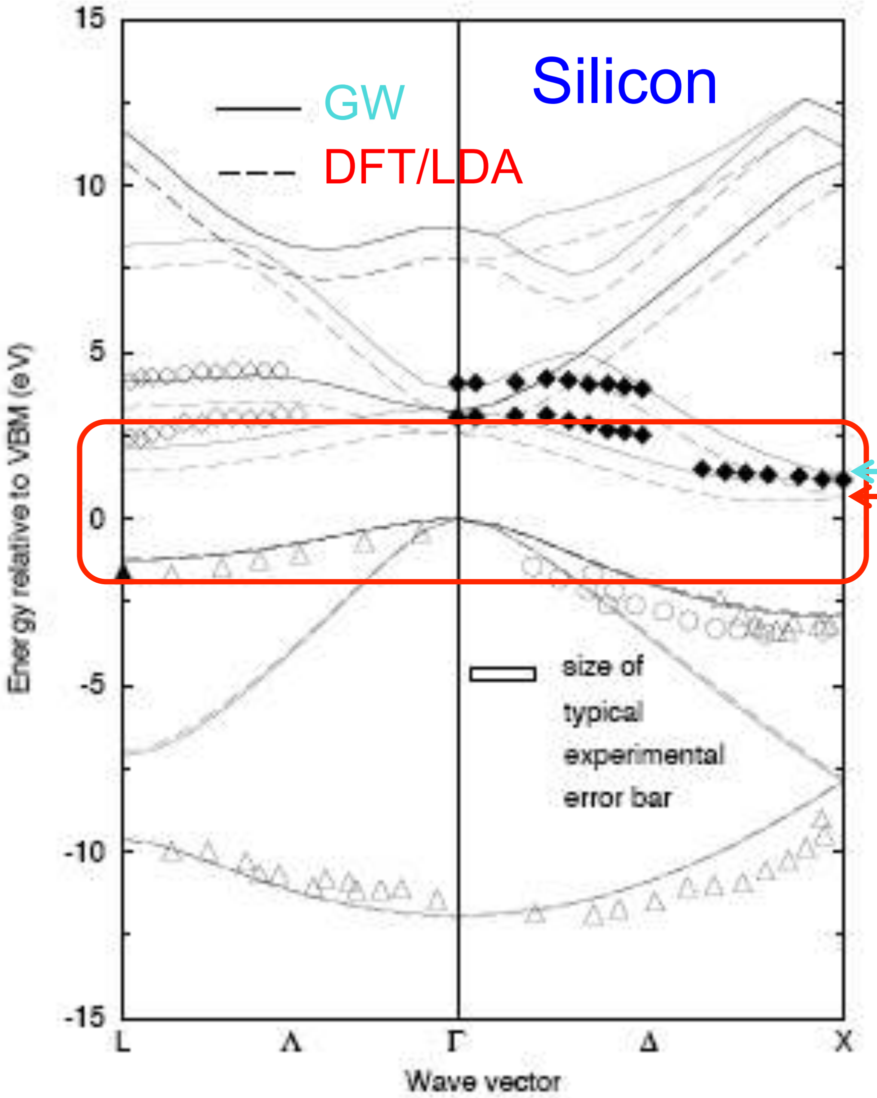


Black : Eu I
Red : Eu II

Absorption geometry,
primitive cell,
4f core-hole + G0W0

Blue : Eu I
Black : Eu II
Red : Eu III

The DFT bandgap problem



Comparison of DFT/LDA and Many-Body Perturbation Theory GW band structures with photoemission and inverse photoemission experiments for Silicon.

Eg (GW)=1.2 eV
Eg (DFT/LDA)=0.6 eV
Eg(exp)=1.17 eV

Problem !

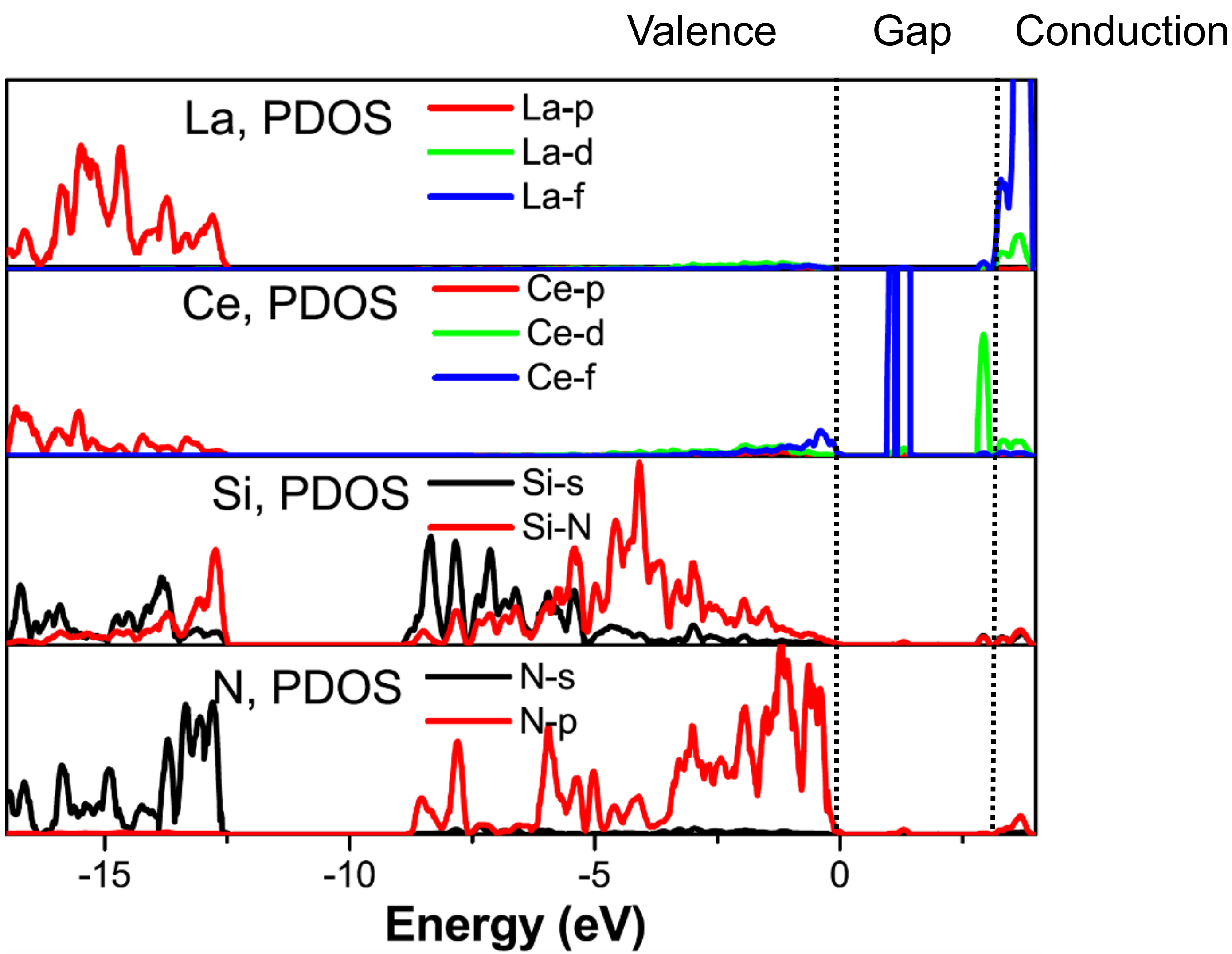
From "Quasiparticle calculations in solids", by Aulbur WG, Jonsson L, Wilkins JW,

Solid State Physics 54, 1-218 (2000)

$La_3Si_6N_{11}$:Ce_{2a} partial Density Of States

A* case

Excited-state Emission geometry



Example : DOE Roadmap

A.1.3 Down Converters		
Description: Explore new regulatory compliant, high-efficiency wavelength conversion materials for improved quantum yield and phosphor conversion efficiency for the purposes of creating warm white LEDs, with a particular emphasis on improving spectral efficiency with high color quality and improved thermal stability. Non-REM (rare earth metal) down converters are encouraged.		
Metric(s)	**2011 Status(s)**	**2020 Target(s)**
Quantum Yield (25°C) across the visible spectrum	90%	95%
Thermal Stability across the visible spectrum – Relative Quantum Yield @ 150°C vs. 25°C	90%	95%
Avg. Conversion Efficiency (pc–LED)	66%	69%
Spectral Full Width Half Max. (FWHM)	150 nm (Red)	<30 nm All colors
Color Stability (pc–LED)	Color Shift 0.012 u'v' over life	Color Shift < 0.002 u'v' over life
Spectral Efficiency relative to a max. LER ~345 lm/W	90%	100%
Flux Density @ 85°C		