Ab initio study of hydration properties in M doped $BaSnO_3$, M = In, Y, Gd, Sm, La

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Introduction

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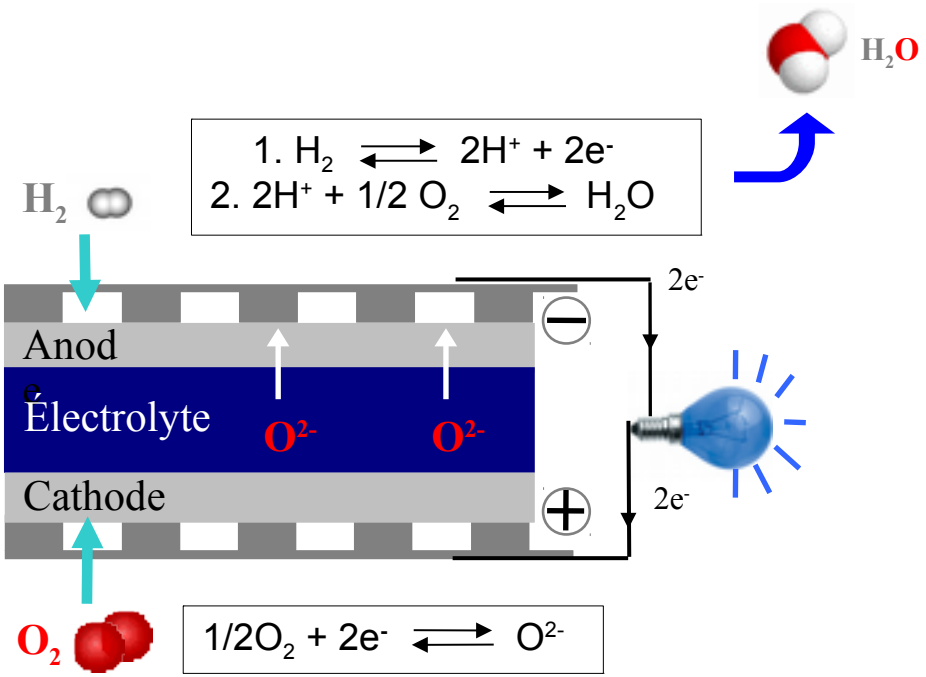
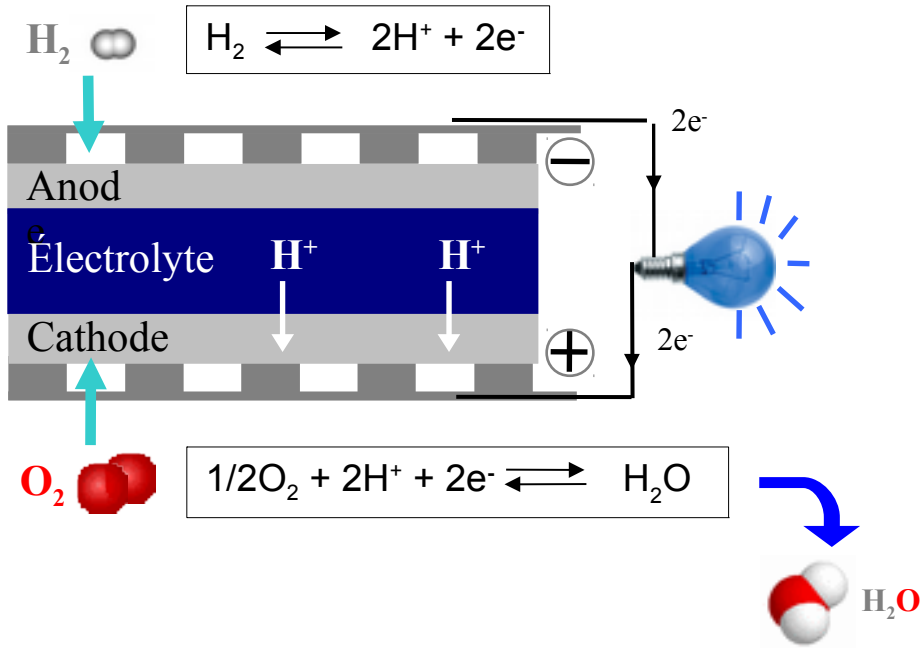
Short introduction

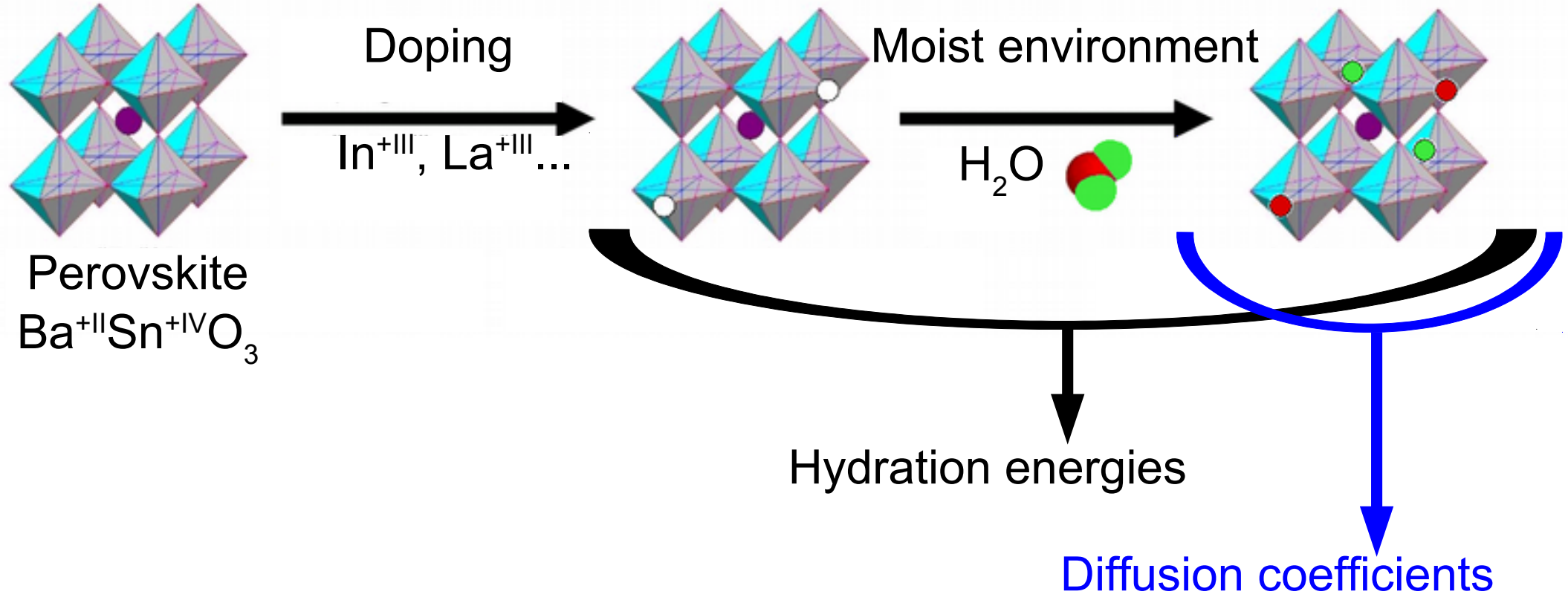




Systematic experimental and theoretical study of this material

T. Schober, Solid State Ionics, **109** (1998) 1-11
Murugaraj *et al*, Solid State Ionics, **98** (1997) 1-11

Short introduction



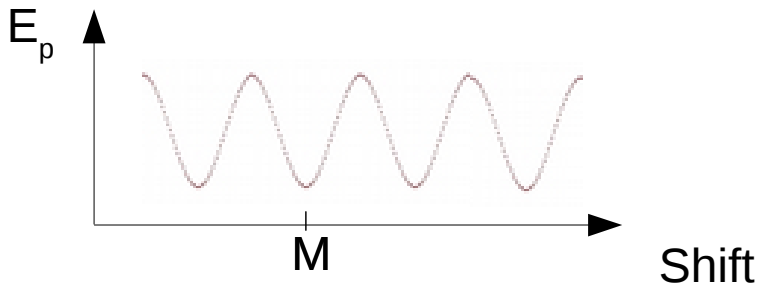
Good protonic conductions are ensured by high hydration energies and high diffusion coefficients.

I. Theoretical part

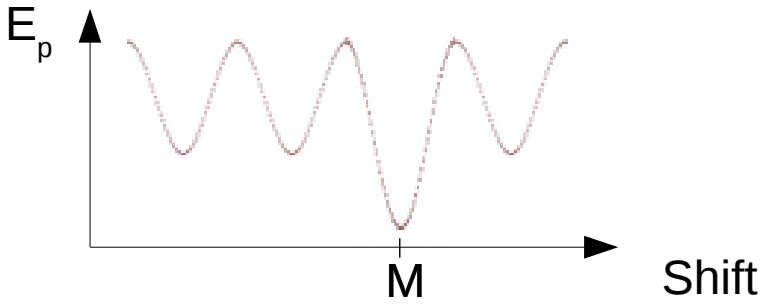
1. Thermodynamic model

Computing hydration energies

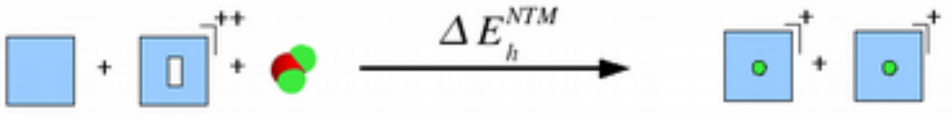
No Trapping Model (NTM)

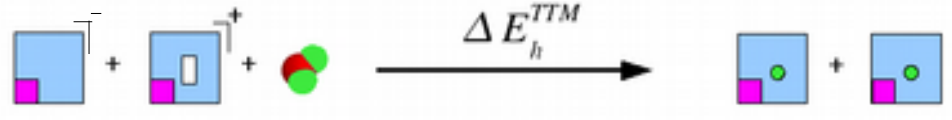


Total Trapping Model (TTM)



$$H_2O(g) + V_o^{\bullet\bullet} + O_o^X \rightleftharpoons 2(OH_o^{\bullet})$$





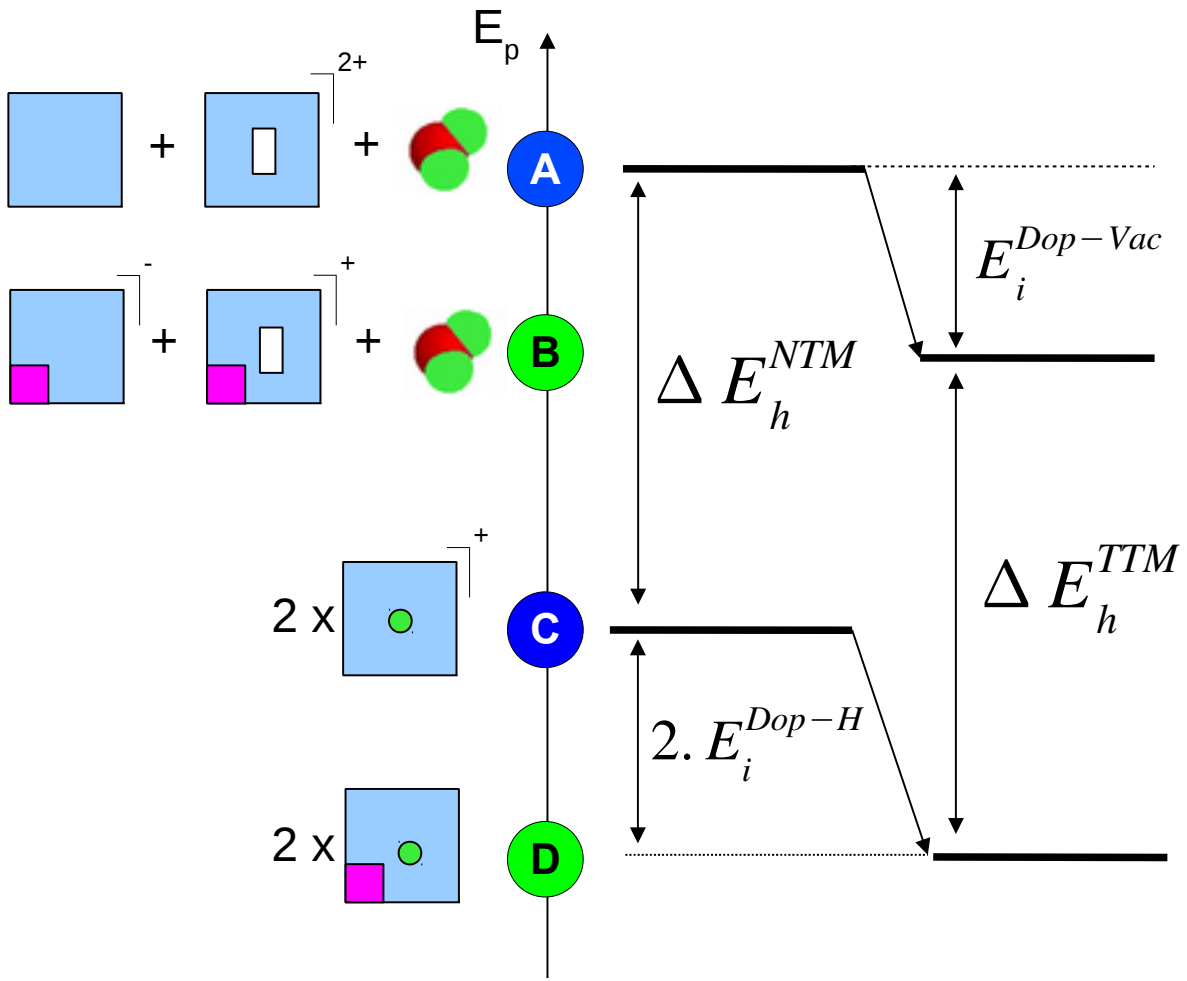
No interactions with dopants:

Intrinsic properties

Interactions with dopants:

Dopant effect
Multiple dopant defect positions

In summary



NTM model:

$\Delta E_h^{NTM} = C - A$

TTM model:

$\Delta E_h^{TTM} = D - B$

Possibility to compute hydration energies but also interaction energies between defects.

I. Theoretical part

2. Computation details

2. Computation details

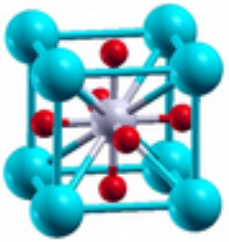
Access to informations from the atomic scale :

- Systems energies
- Optimized geometries at ground state
- Vibration frequencies at ground state
- Molecular dynamics

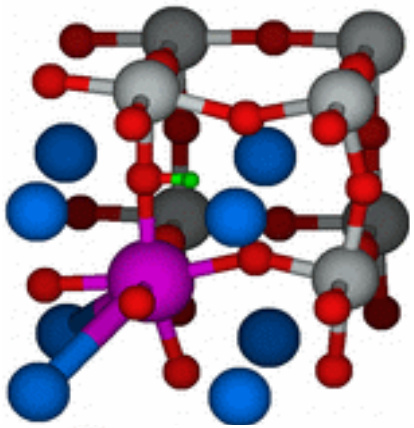
Computations features

- Codes : Abinit / SIESTA
- Methods : Density Functional Theory (DFT)
- Functional GGA PBE
- Pseudopotentials : Troullier-Martins

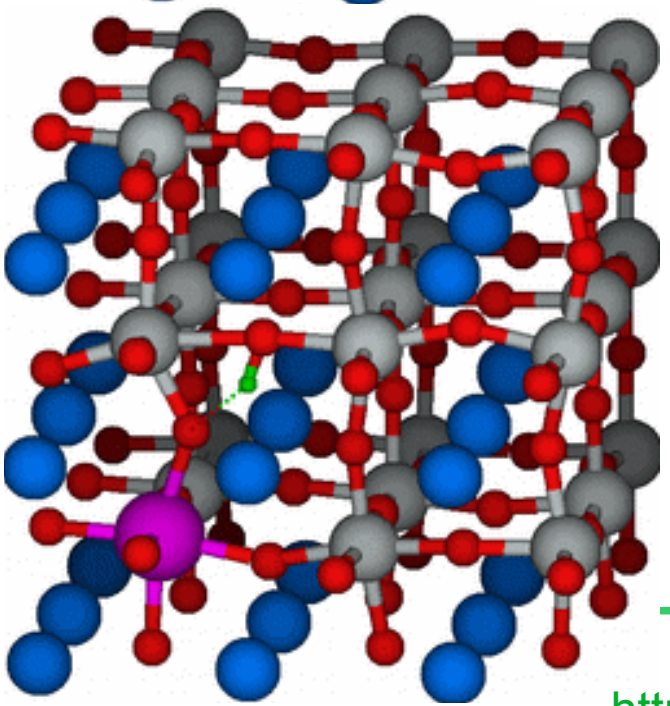
2. Computation details



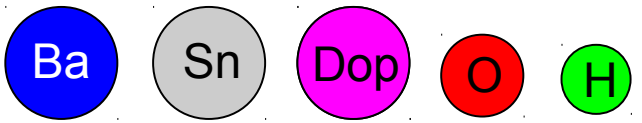
Elementary cell. Impossibility to modelize defects (Abinit and SIESTA)



Asymmetric 2x2x2 supercell, defect modelized with a dopant concentration of 1/8, 12,5%. But dopant images effect. (SIESTA & Abinit)



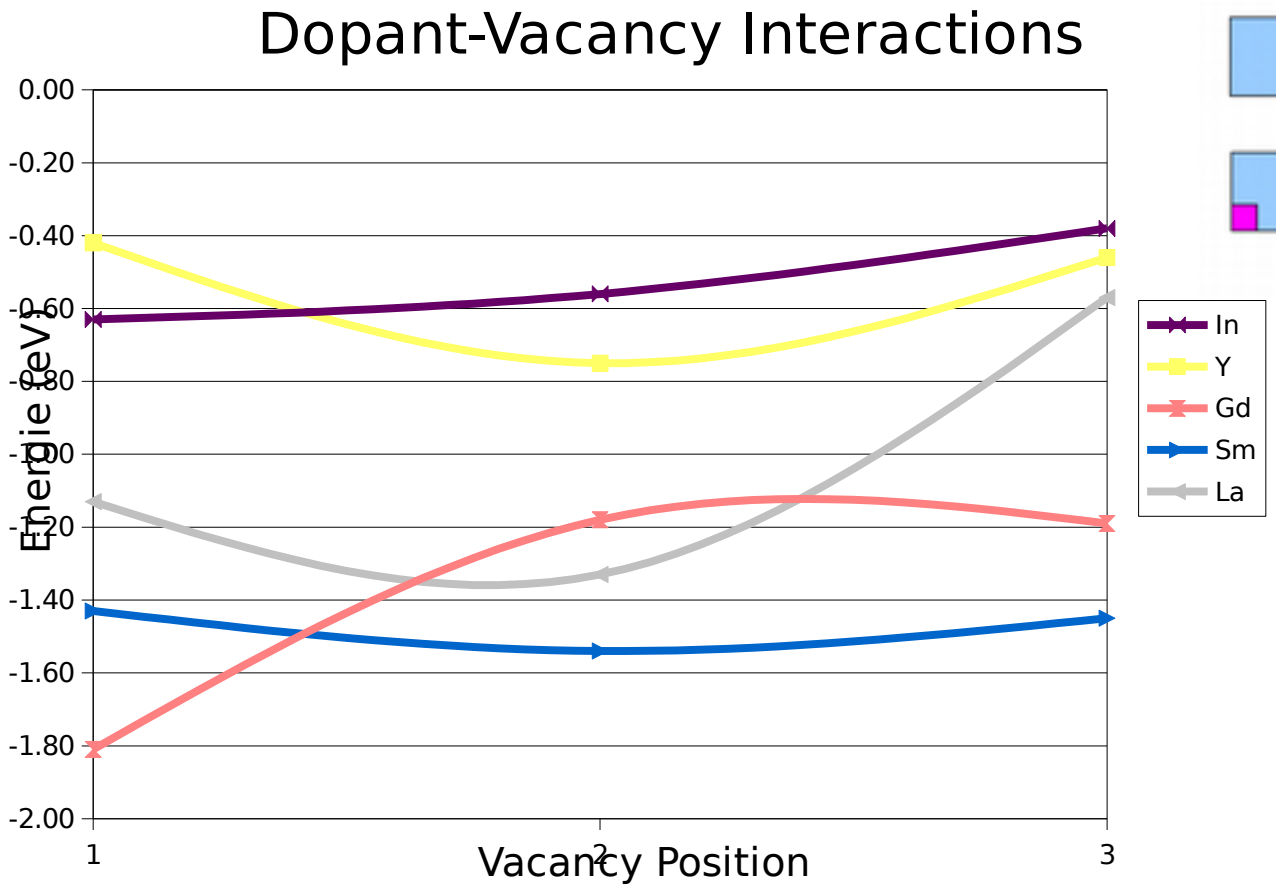
Asymmetric 3x3x3 supercell, defect modelized with a dopant concentration of 1/27, ≈ 3,7%. No effect of dopant images (SIESTA).

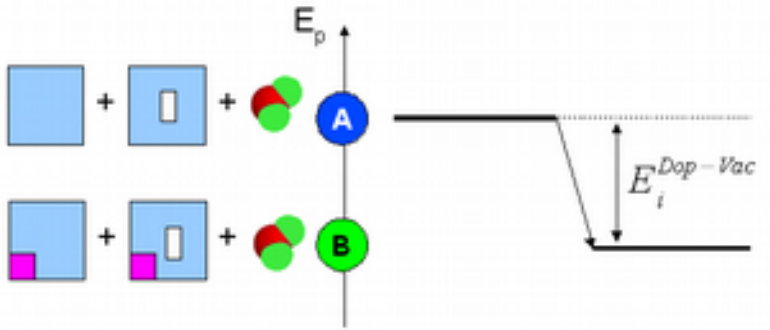


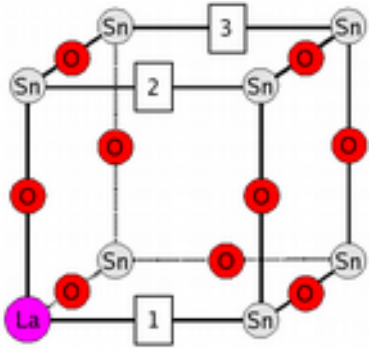
II. Results

1. Abinit results, supercell 2x2x2 (Sc222)

Dopant-Vacancy Interaction (Abinit Sc222)







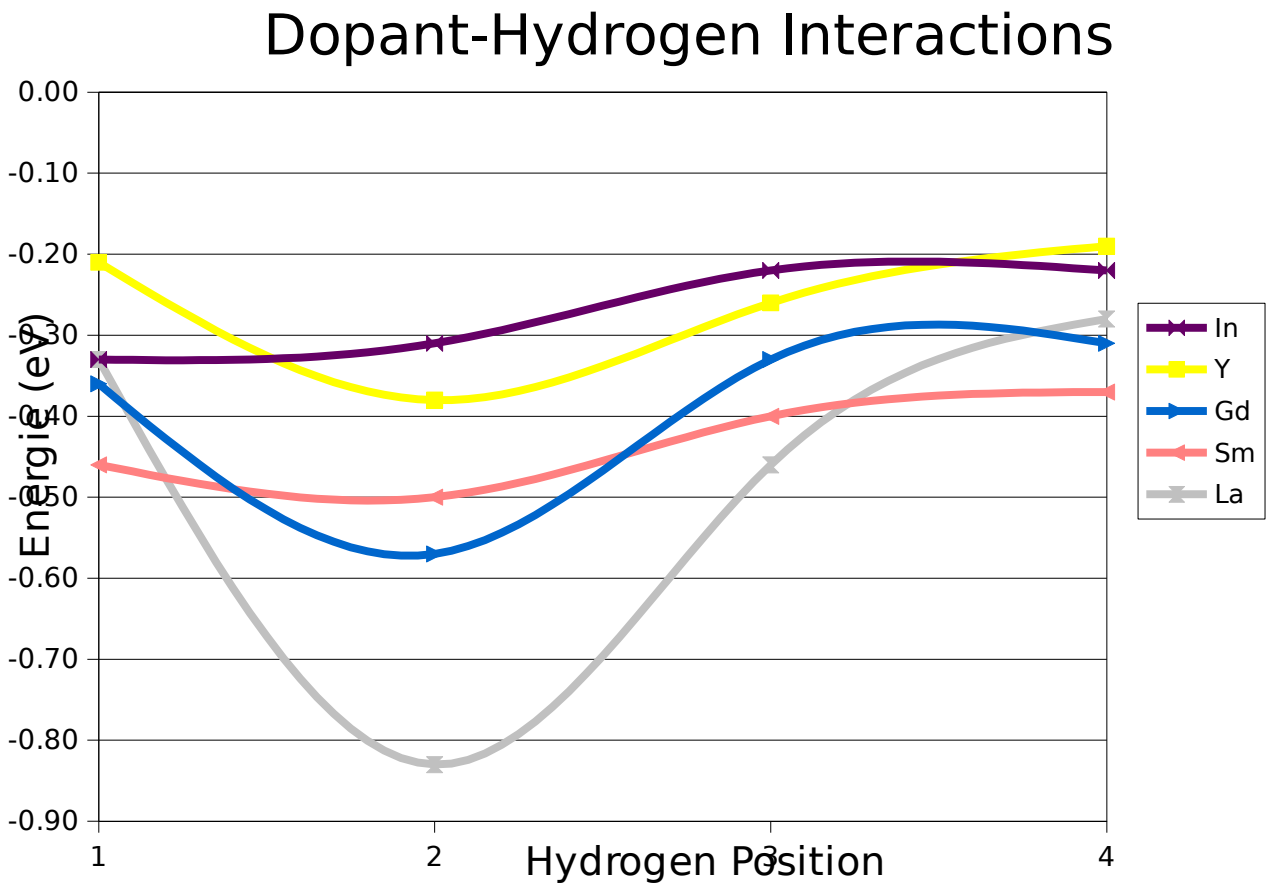
In, Y : low interaction energy

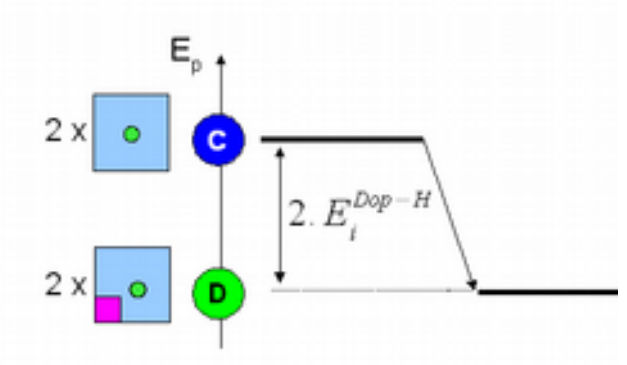
Gd, Sm, La : strong interactions energies, may reduce hydration energies

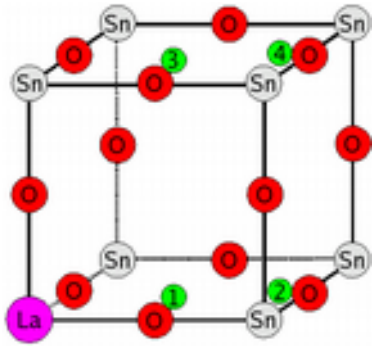
Strong variation function of the position of the vacancy

E. Bévillon, G. Geneste *et al.* (2008) *Ionics 14:4*
E. Bévillon and G. Geneste, (2008) Phys Rev B 77:184113

Dopant-Hydrogen Interaction (Abinit Sc222)







Indium : POS1 the most stable position, and the most flat curve
Others : POS2 the most stable positions
Y, Gd and La : very strong changes

E. Bévillon, G. Geneste *et al.* (2008) *Ionics 14:4*
E. Bévillon and G. Geneste, Phys. Rev. B 77, 184113 (2008)

Hydration Energies (Abinit Sc222)

	Hydration Energies (eV)			
Dop | Disp	POS1 --> POS1	Strongest	Experiments	
None : NTM	-0,69		na	
In	-0,71	-0,71	-0,76	BISO (50%)
Y	-0,69	-0,70	-0,62	BYSO (10%)
Gd	0,40	-0,02	na	
Sm	-0,16	-0,14	na	
La	-0,22	-1,02	na	

In, Y and La lead to stronger hydration energies than the host material

Gd and Sm, weaker hydration energies, due to strong competition with the lacunar state

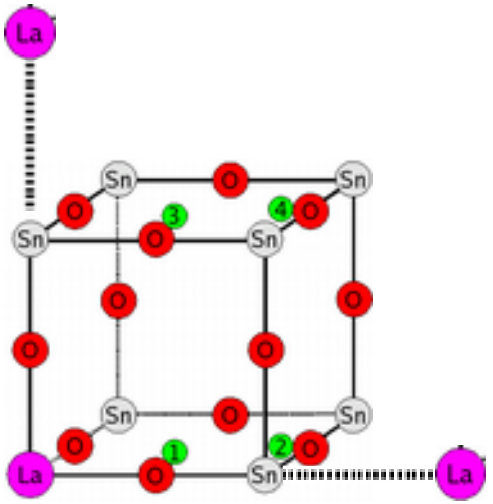
Dependence to the position of the defects

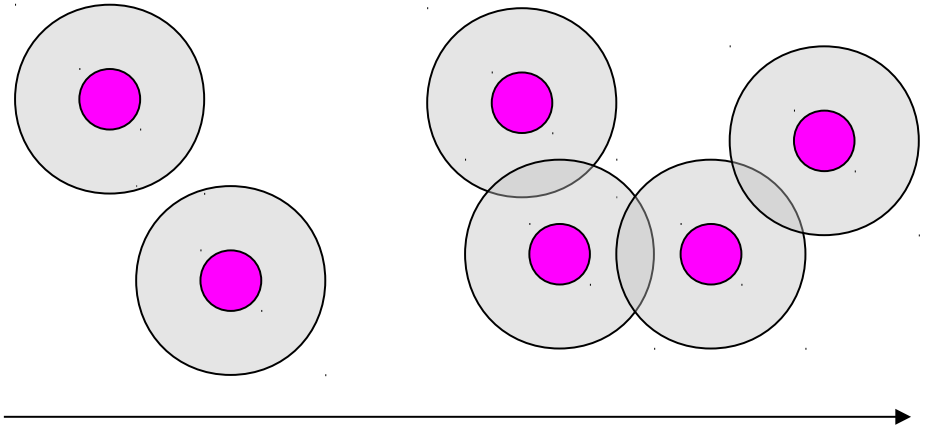
Too few experimental data to conclude on the method

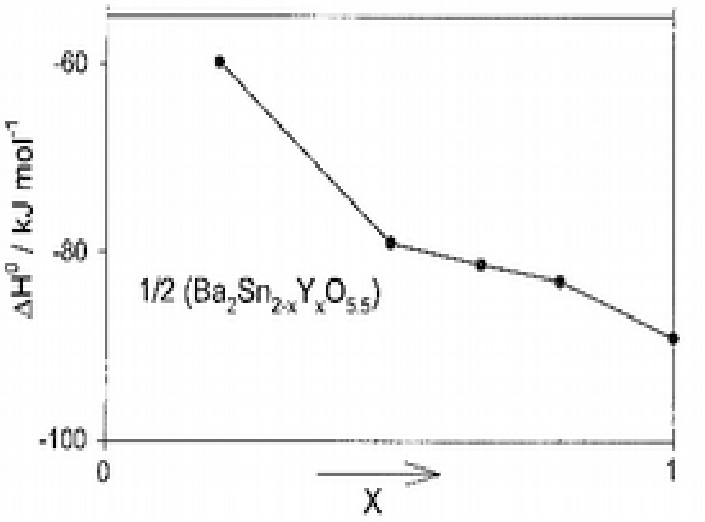
E. Bévillon, G. Geneste *et al.* (2008) *Ionics 14:4*
E. Bévillon and G. Geneste, Phys. Rev. B 77, 184113 (2008)

II. Results
2. Discussion on POS2

POS2, most stable position?





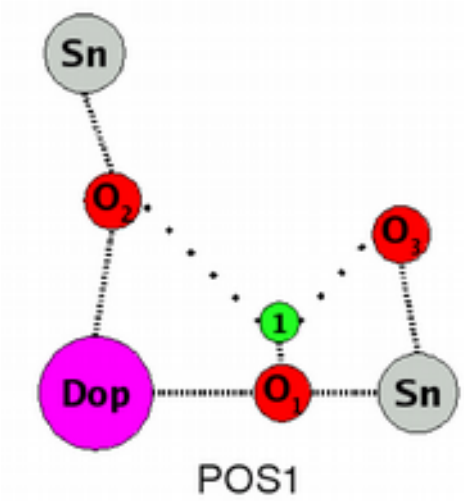


(idem $BaCeO_3$)

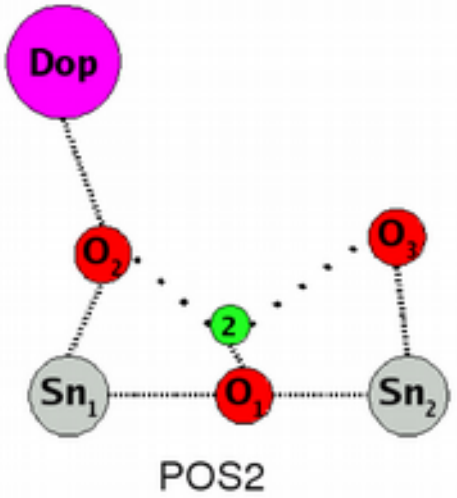
Concentration effect, due to :
- Interactions overlap ?
- Local electronic enrichment of the material ?

Kreuer, Solid State Ionics, **125**, (1999), 285

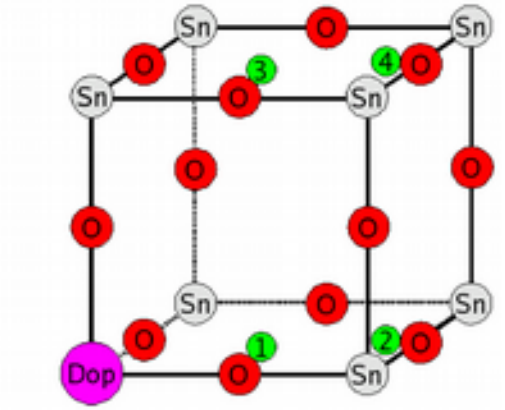
POS2, most stable position?

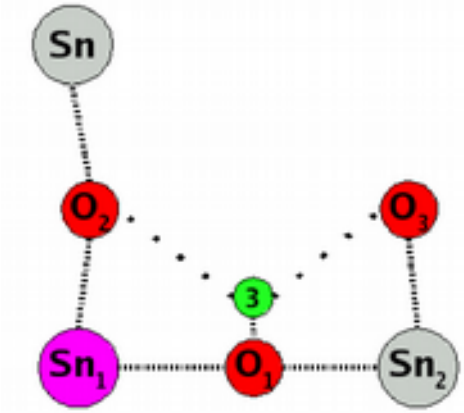


POS1

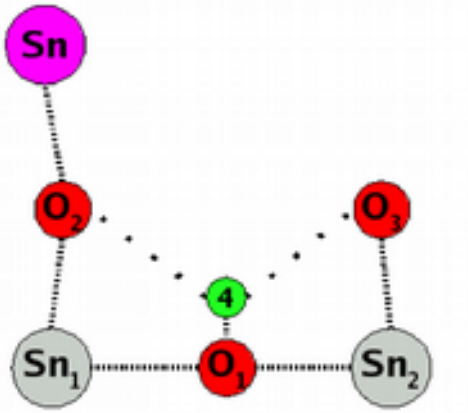


POS2





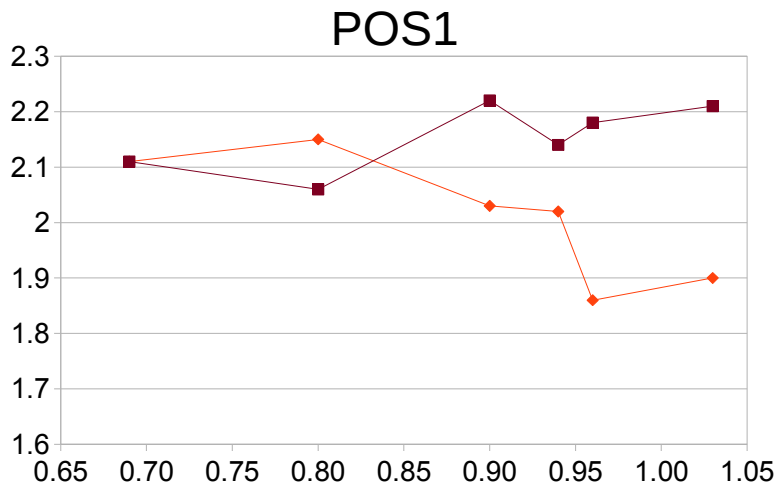
POS3

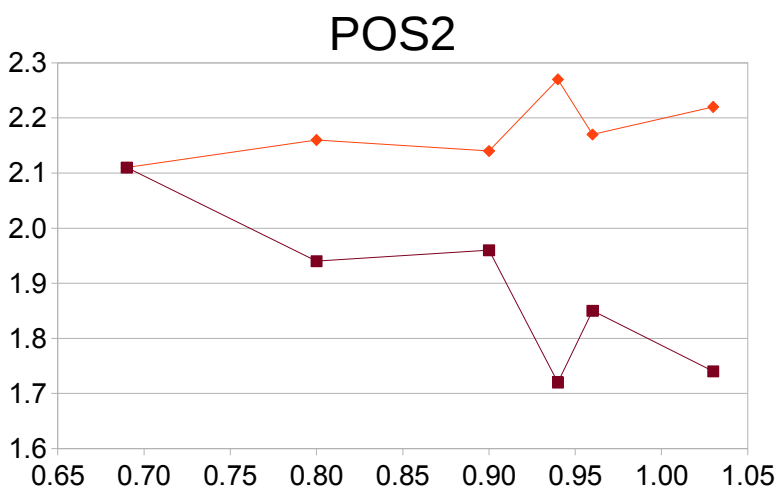


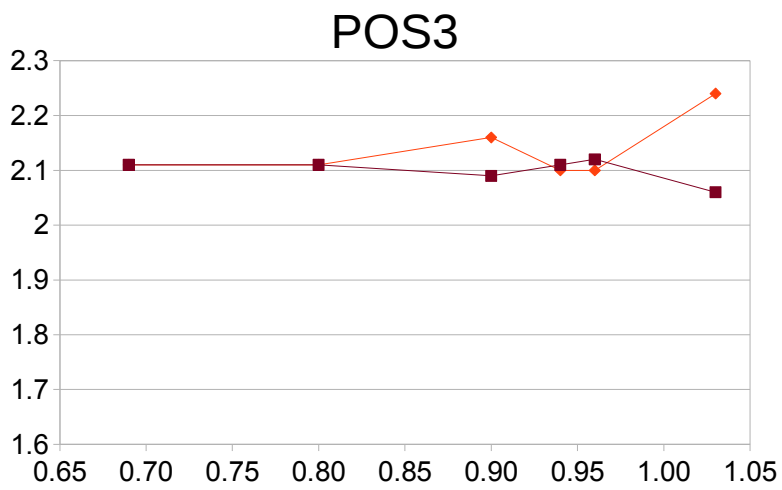
POS4

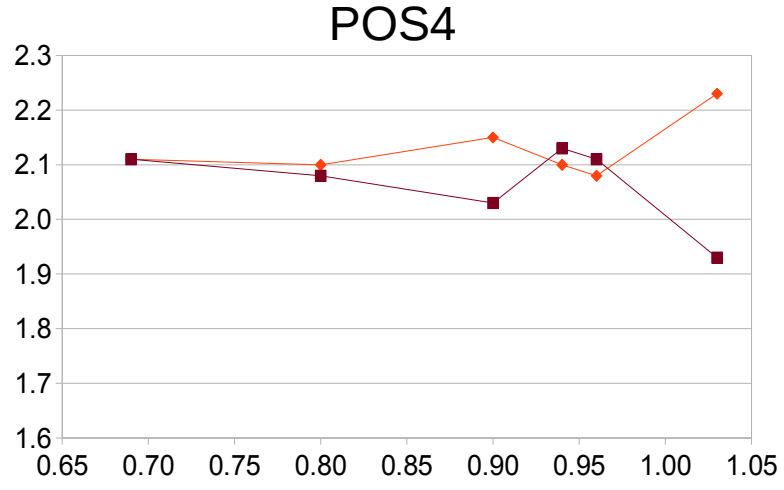
Or structural effect due to the size of the dopant ?

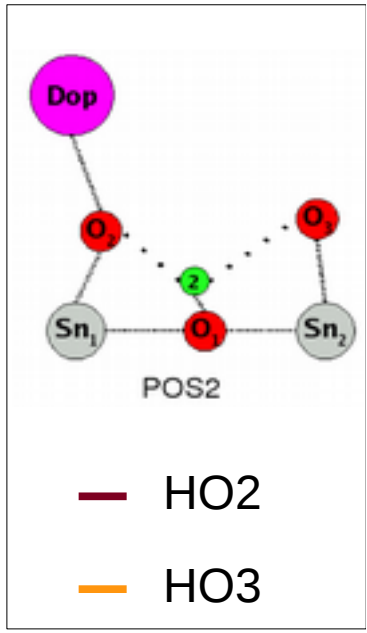
Hydrogen bond analysis









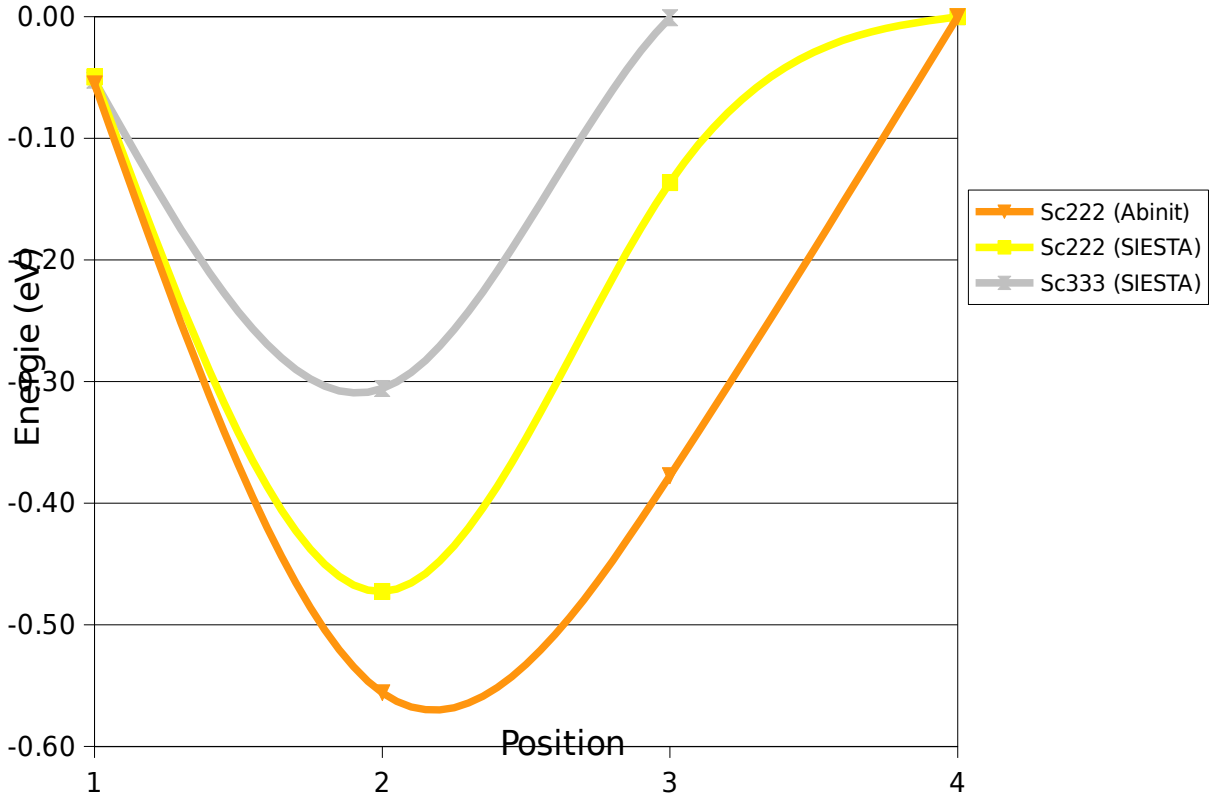


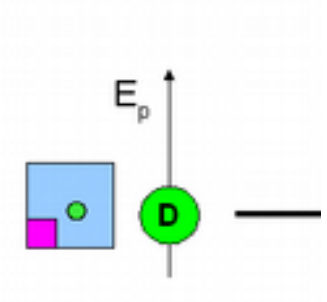
Shannon radius of the dopant

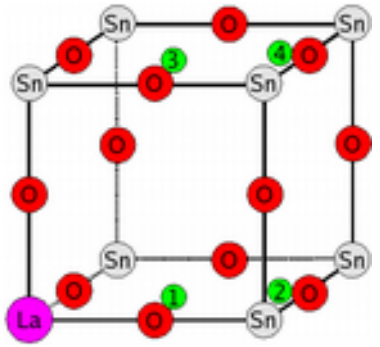
POS1 - POS2 strong distortions; POS2 : Hydrogen bonds appear with big dopants.

Relative energies (Abinit & SIESTA)

Relative energies of systems containing La and H



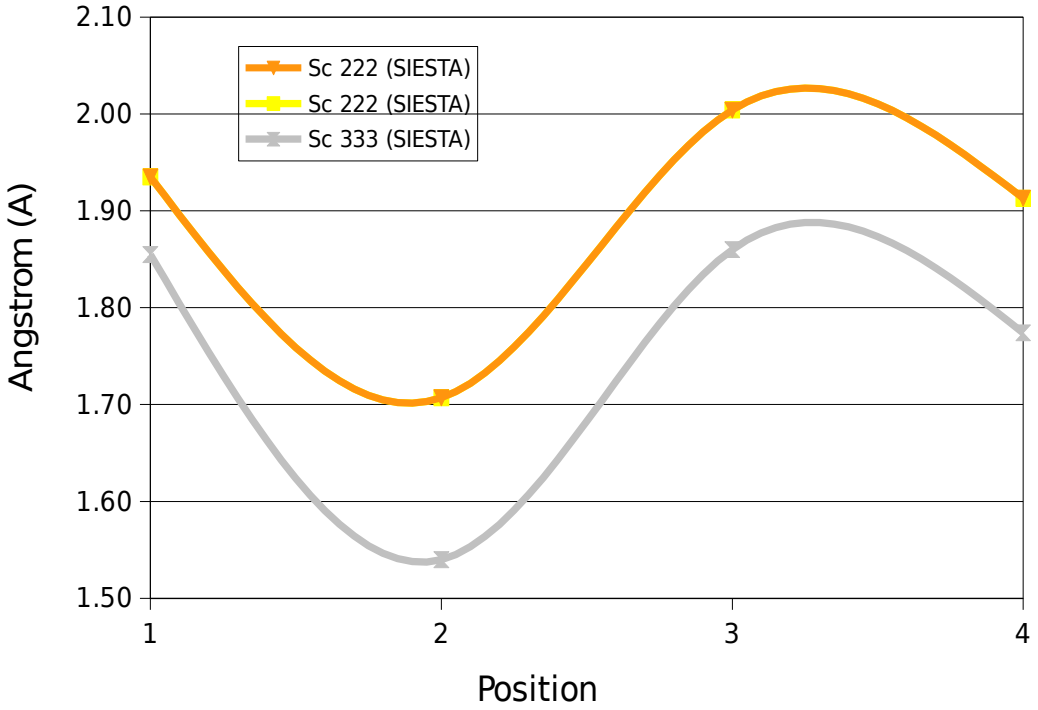


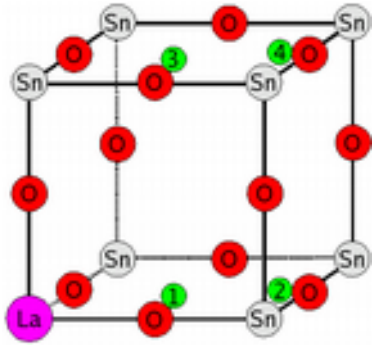


POS2 still lead to the most stable position
It is to notice that the intensity is less high in Sc333 than in Sc222
In the case of La, computations lead to close results for Sc222

Hydrogen bond analysis (Abinit & SIESTA)

Shortest hydrogen bond, systems containing La and H





Hydrogen bonds vary along the same tendency, function of the hydrogen position

POS2 always exhibit the shortest Hydrogen bond distances, whose stabilize more the whole system in POS2.

Conclusion

Conclusion

Hydration energies computed, but lack of experimental data to confirm the validity of the method.

Interaction energies or relative energies exhibit a size effect with big dopants which lead POS2 as the most stable position. This is of interest still up till now only POS1 was computed.

The hypothesis of a dopant concentration is not invalidated and the way it acts is still to be studied.

Energy barriers are also currently studied in order to modelize Hydrogen pathway inside of the whole 12,5% doped simulated material.

Also computations with SIESTA with other dopants are currently running, computation of hydration and interaction energies have to be done for Sc222 and Sc333.

Thanks for attention

The End