Ab initio study of hydration properties of doped $BaSnO_3$, as a proton conductor

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Synopsis

Introduction

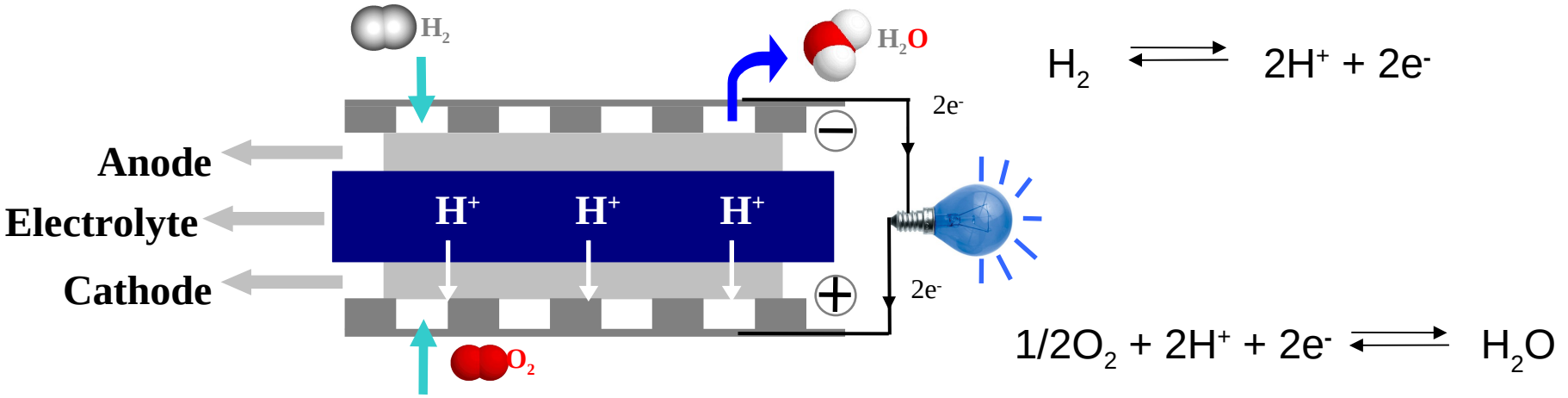
Part 1: Theoretical background

Part 2: Results and hydration energies estimation

Conclusion

Introduction

Doped $BaSnO_3$: a good candidate for electrolyte of fuell cell as a protonic conductor. T. Schober, Solid State Ionics, **109** (1998) 1-11. Murugaraj *et al*, Solid State Ionics, **98** (1997) 1-11



--> Systematic theoretical and experimental investigation of doped $BaSnO_3$ in our group

Computational details

Code used: Abinit

Methods: DFT

Functional: GGA PBE

Pseudopotentials: Troullier-Martins

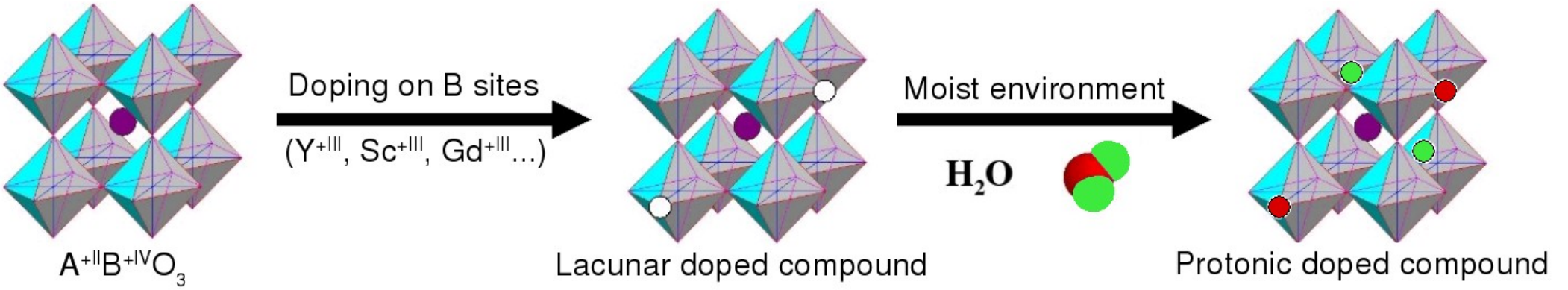
2x2x2 charged supercell used (±40 atoms)

Brillouin zone sampling: 2x2x2

Plane waves cut off: 30 Hartree

Part 1: Theoretical background

Our aim? Computing hydration energy of the doped materials



$$[OH] = \frac{3.K^{o}.P_{H2O} - \sqrt{K^{o}.P_{H2O}.(9.K^{o}.P_{H2O} - 6.K^{o}.P_{H2O}.[Dop] + K^{o}.P_{H2O}.[Dop]^{2} + 24.[Dop] - 4.[Dop]^{2})}}{[Dop].(K^{o}.P_{H2O} - 4)}$$

Formula

$$K_h^o(T) = \exp\left(\frac{-\Delta G_h^o(T)}{k_b.T}\right)$$

$$\Delta G_h^o(T) = \Delta H_h^o(T) - T\Delta S_h^o(T)$$

$$\Delta H_h^o(T) = \Delta E_h^o(T) + P\Delta V^o(T)$$

Approximations used

$\Delta S_h^o(T)$ non accessible

$\rightarrow \Delta S_h^o(T)$ fixed value

$P\Delta V^o(1200\text{K}) \approx k_b T = 0{,}1\, eV/H_2O$

$\rightarrow \Delta H_h^o(T) \approx \Delta E_h^o(T)$

Ellingham approximation

$$K^o(T) = \exp\left(\frac{-\Delta G^o(T)}{k_b.T}\right)$$

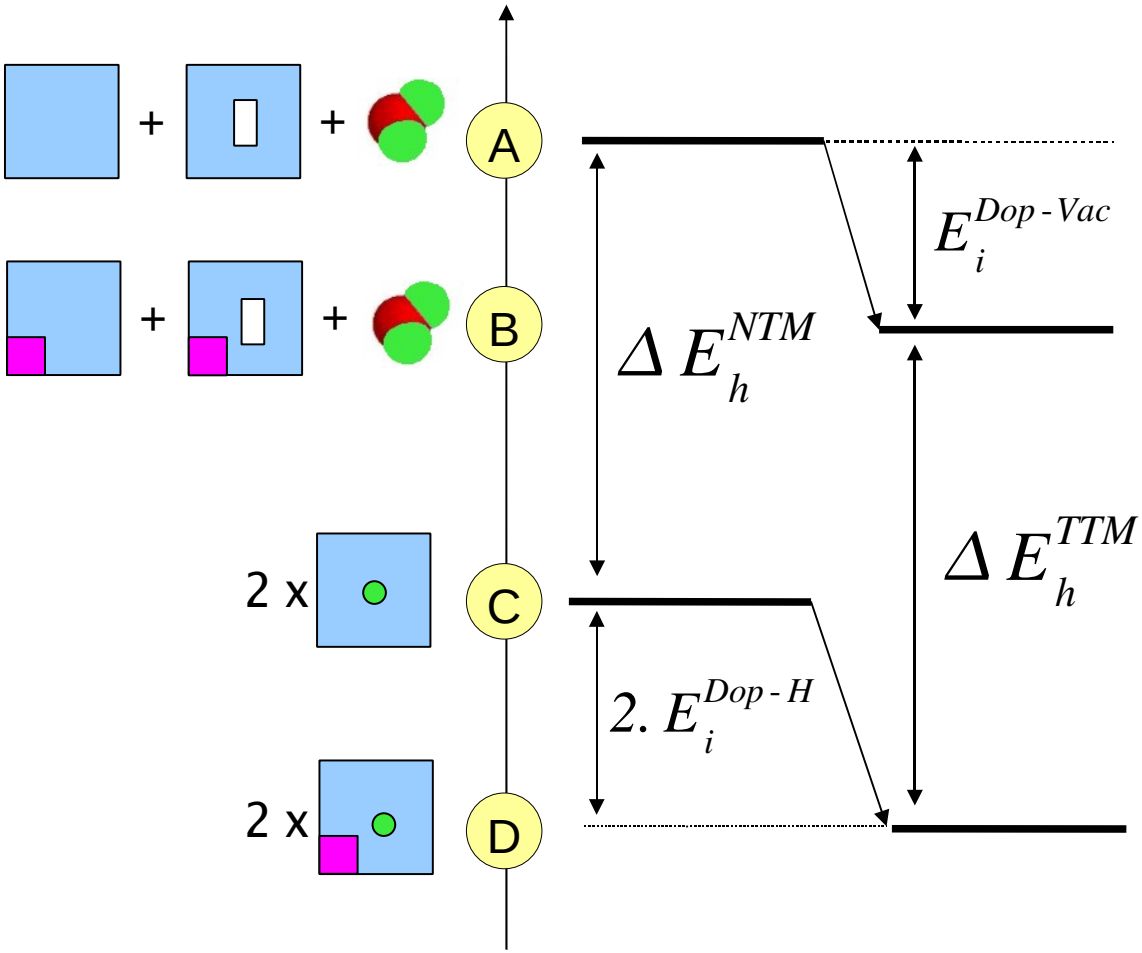
$$\Delta G_h^o(T) = \Delta H_h^o - T\Delta S_h^o$$

$$\Delta H_h^o \approx \Delta E_h^o$$

How to compute the hydration energy (ΔE_h) ?

No Trapping Model (NTM) and Total Trapping Model (TTM)

M. E. Bjorketun *et al,* Faraday Discuss., **134,** 2007, 245-265



NTM model:

Dopant Vacancy and Dopant

Proton interactions neglected.

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

TTM model:

Dopant Vacancy and Dopant

Proton interactions considered.

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

Part 2: Results and hydration energies estimation

-NTM Model- Hydration energies

(Hypothesis: weak interactions with dopants and/or low dopant concentration.)

$$\Delta E_h^{NTM}\ BaSnO_3 = -0{,}96\ eV$$

$$\Delta E_h^{NTM}\ BaZrO_3 = -0{,}79\ eV$$

* M. E. Bjorketun *et al,*

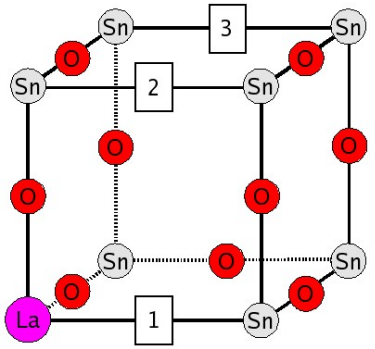
Faraday Discuss., 2007, 245-265

--> From this simple approach, $BaSnO_3$ would exhibit a slightly better hydration than $BaZrO_3$.

-TTM Model- Dopant-Vacancy interaction (eV)

(Hypothesis : Dopant-Vacancy interactions strong enough to imply their proximity (POS1))

	$BaSnO_3$	$BaZrO_3$ *
Dopant	POS1	POS1
Ga	-2,92	-0,68
In	-0,16	-0,62
La	-1,47	-
Sm	-2,03	-
Gd	-2,38	-0,55



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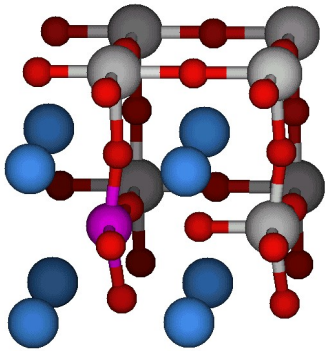


Ga doped, POS1

Optimized structure

--> Distorted structure in Ga case.

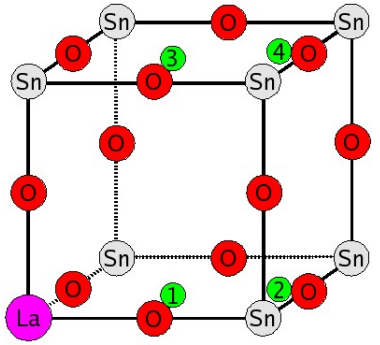
--> Exception of the In dopant

--> Strong dopant vacancy interaction

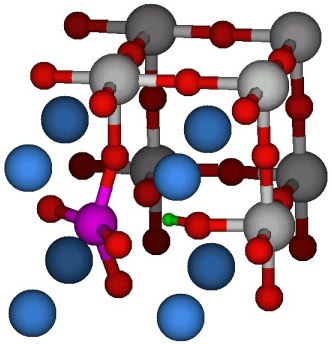
-TTM Model- Dopant-Proton interaction (eV)

(Hypothesis : Dopant-Proton interactions strong enough to imply their proximity (POS1 & POS2))

	$BaSnO_3$		$BaZrO_3$ *
Dopant	POS1	POS2	POS1
Ga	-2,31	-0,45	-0,38
In	0,04	0,06	-0,20
La	-0,31	-0,81	-
Sm	-0,58	-0,62	-
Gd	-0,50	-0,71	-0,14



* M. E. Bjorketun *et al*, Faraday Discuss., 2007, 245-265



Ga doped, POS1
Optimized structure

--> Gallium, distorted structure in POS1

--> Indium, no big difference with Sn

--> Interactions generally stronger in POS2 case

-TTM Model- Hydration energies (eV)

	$E_i^{Dop-Vac}$	$2.E_i^{Dop-H}$		Hydration energy (eV/H20)		
Dopant	POS1	POS1	POS2	BaSnO3 (1)	BaSnO3 (2)	BaZrO3
Ga	-2,92	**-2,31**	**-0,45**	**-2,66**	**1,06**	-0,86
In	-0,16	**0,04**	**0,06**	**-0,72**	**-0,68**	-0,57
La	-1,47	**-0,31**	**-0,81**	**-0,13**	**-1,11**	-
Sm	-2,03	**-0,58**	**-0,62**	**-0,1**	**-0,17**	-
Gd	-2,38	**-0,50**	**-0,71**	**0,41**	**0,00**	-0,51

POS1:

--> Gallium: a very strong hydration energy is found

--> Indium: would hydrate quite well

--> Rare earth elements: weak or positive hydration energies

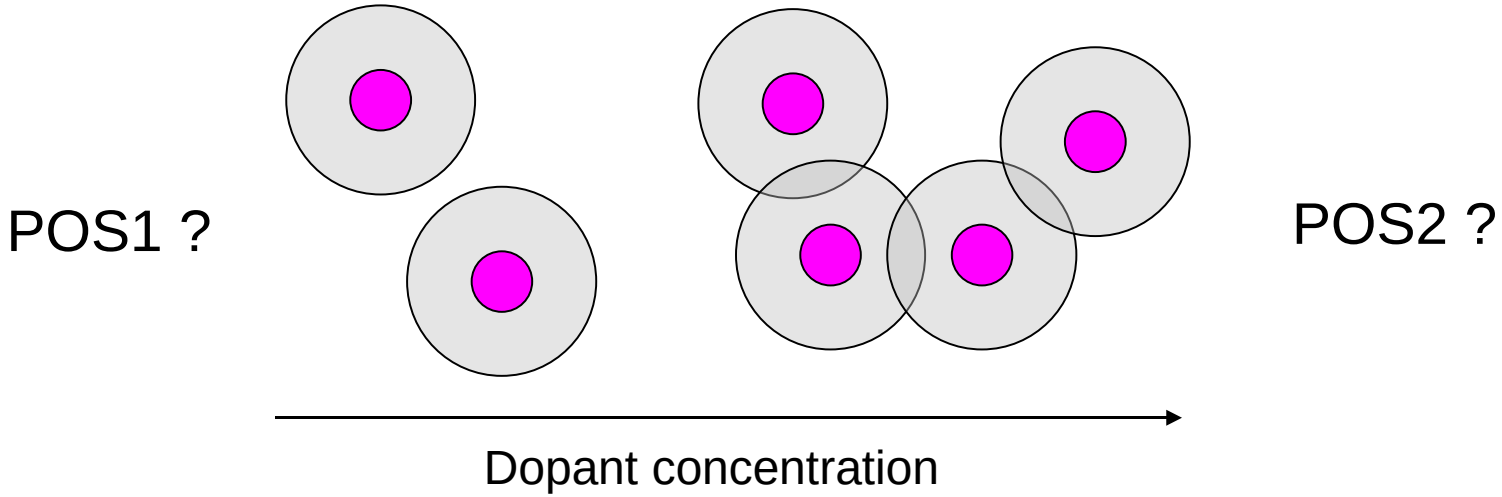
POS2:

--> Gallium: strong positive hydration energy.

--> Indium: no change

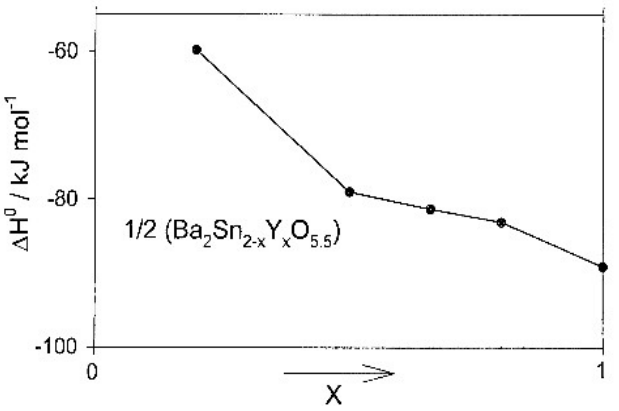
--> Rare earth elements: shift to negative values (quite good for the La)

Discussion: Overlap of the dopant proton interactions ?



--> POS2 can be more stable POS1, for [X] = 12,5%: interaction go further than the first neighbour. Reason why the hydration energy becomes more negative with [X] ?

Kreuer, Solid State Ionics, 125, 1999, 285



Conclusion: work in progress

--> Better refinement of the models

--> Larger supercell calculations (3x3x3 supercells) to confirm the possible overlap of interactions.

--> Computations using different dopants

--> Comparison with experiments