Protons & Dopants in Oxide Materials

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Chemistry, Surrey
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Outline

- **Background & Methods**
- **Proton conductors: $AZrO_3$; $ACeO_3$ perovskite-type**
  - ***Proton transport***
  - ***Dopant sites***
  - ***Proton-dopant interactions***
  - ***Non-stoichiometry***
- **Summary**


LONDON
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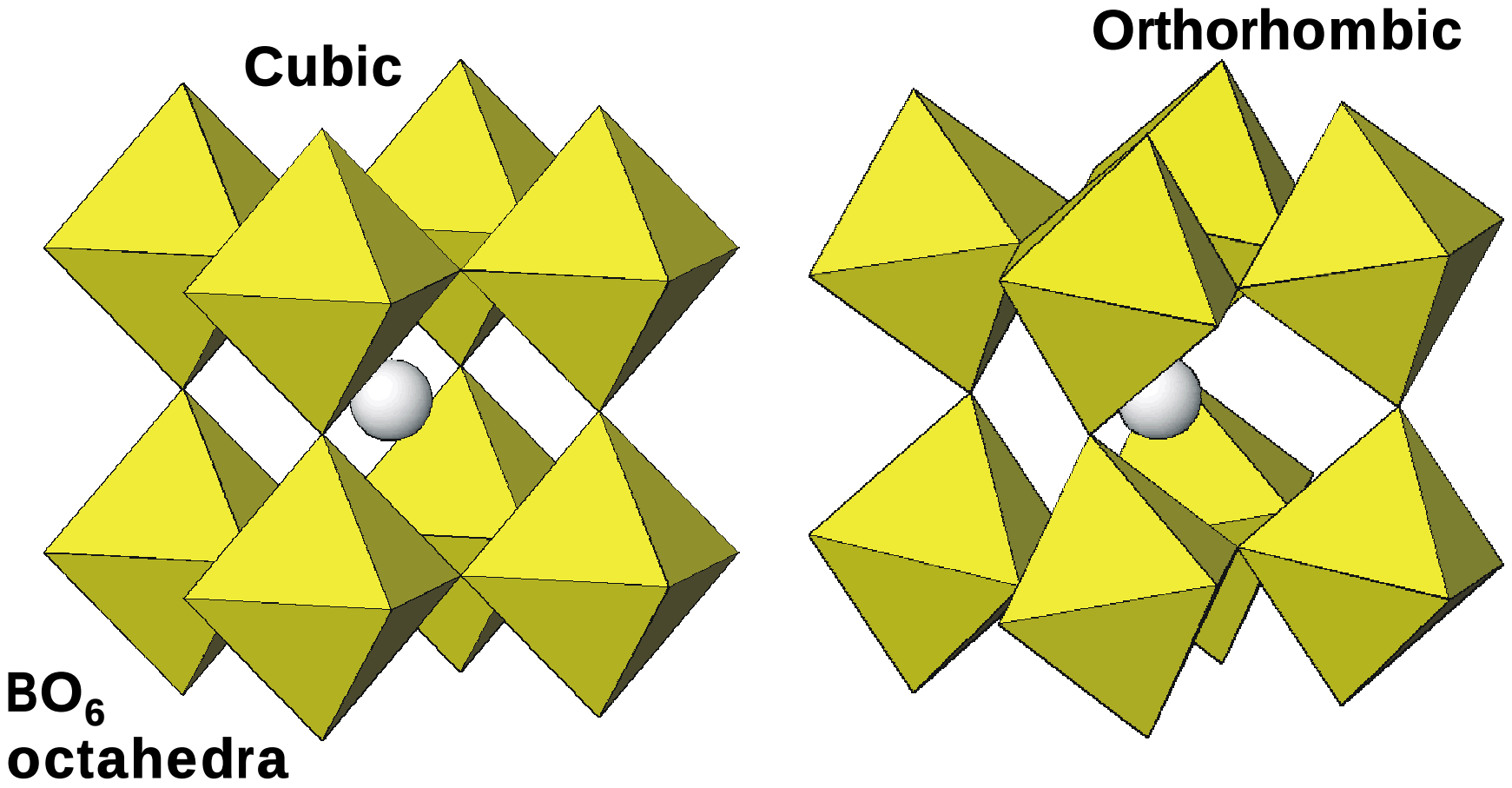
GATWICK
AIRPORT
SOUTHAMPTON
ENGLISH CHANNEL

Background&Methods

Perovskite Structure (ABO_3)

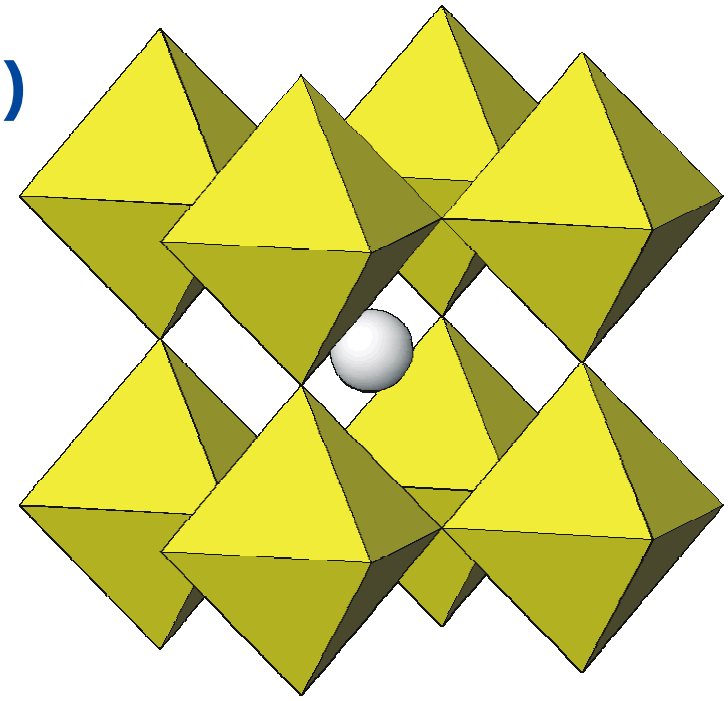


"Inorganic chameleon" - rich variety of properties

Perovskites: Proton Conduction

Fuel cells: intermediate T (< 800˚C)

Sensors



- **Zirconates: $CaZrO_3$, $BaZrO_3$**
- **Cerates: $SrCeO_3$, $BaCeO_3$**
- **Doped e.g. Y, Yb, In**

e.g. Iwahara, Norby, Kreuer, Haile

$$H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^x \rightarrow 2OH_O^{\bullet}$$

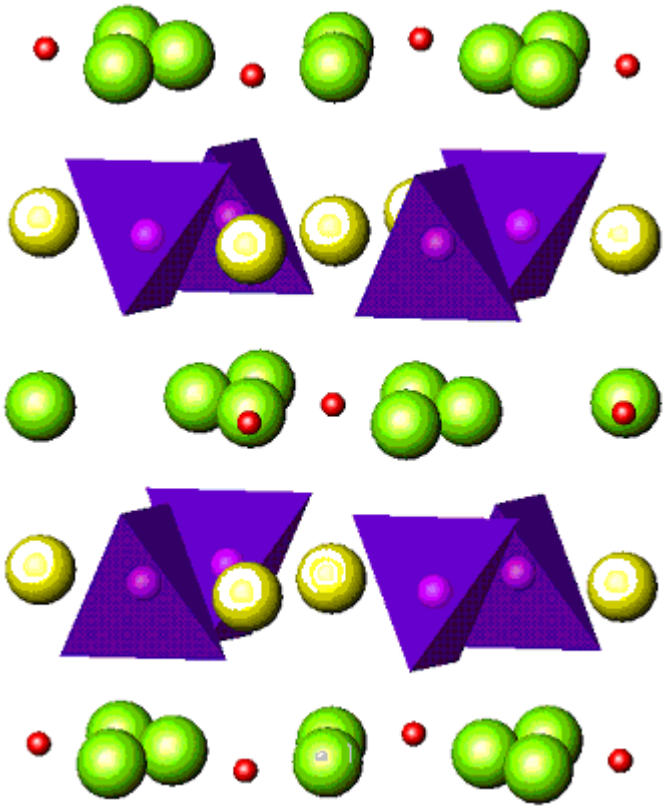
Other Oxides

- **Recent work on other proton-conducting oxides**

  (Norby, Bonanos, Irvine, Slater)

- **Doped $LaScO_3$**

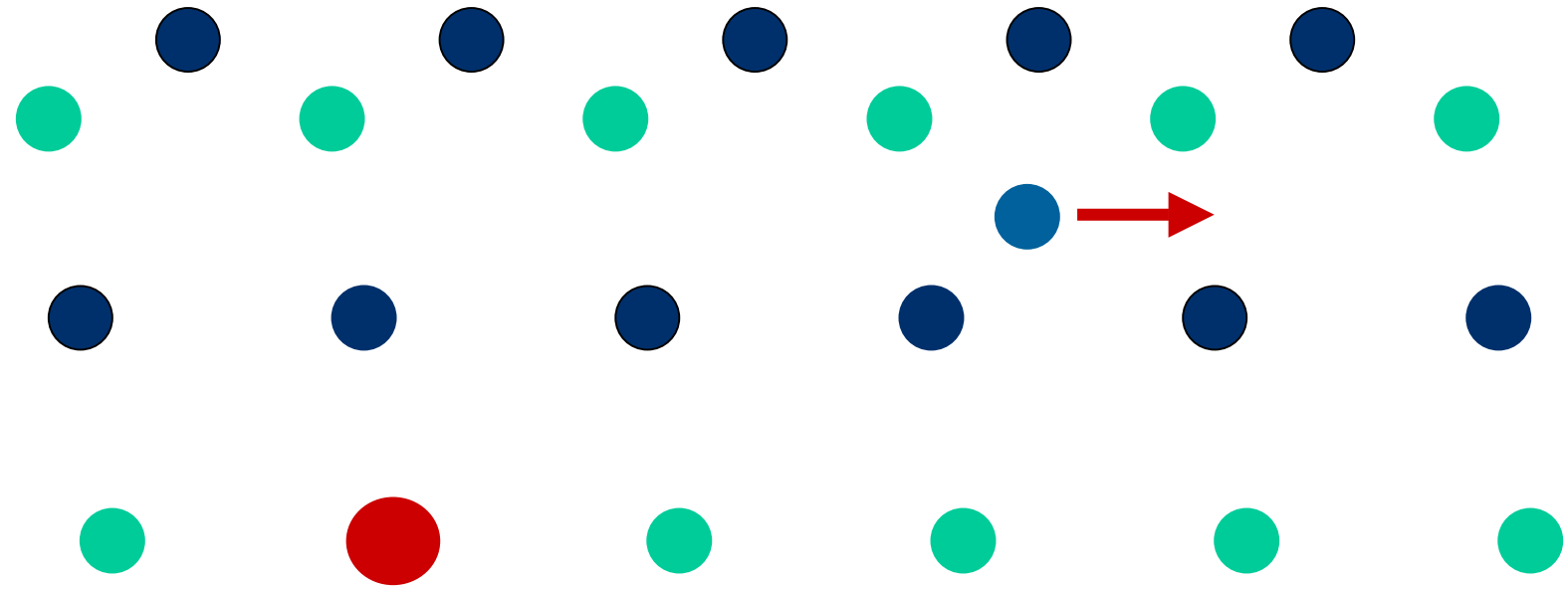
- **$LaBaGaO_4$; $LaSrGaO_4$ (Tetrahedral Ga)**



P. Slater, Chem. Comm., 2003

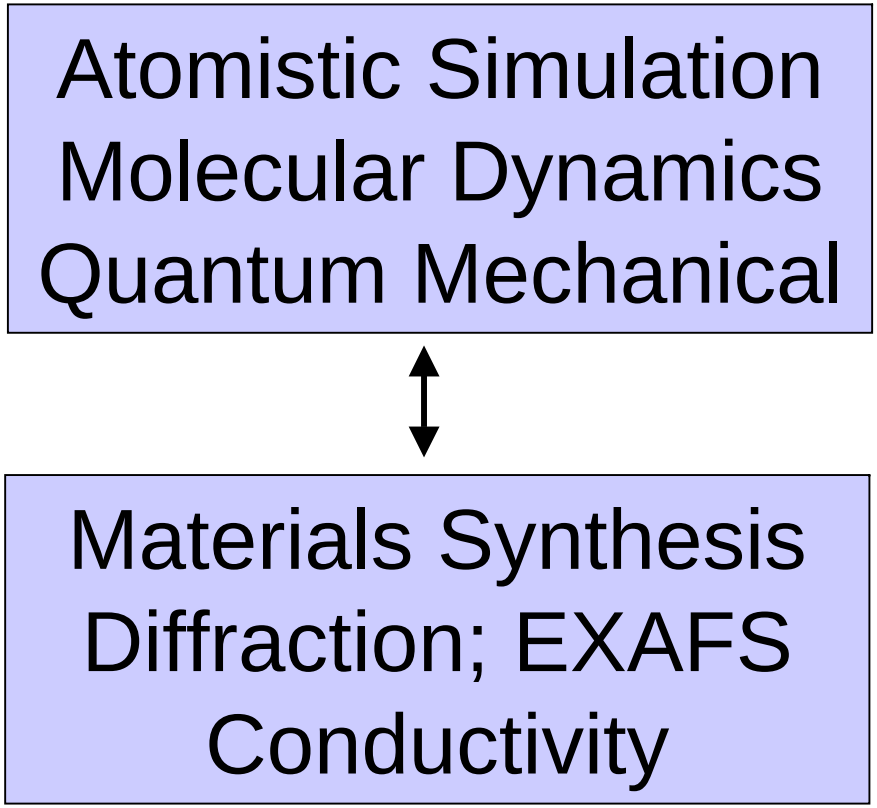
Solid State Questions

Structure-property relationships on atomic & nano-scale



Defects, ion migration, dopants, clustering, surfaces

How? Interdisciplinary Approach



- **Modelling Aims**

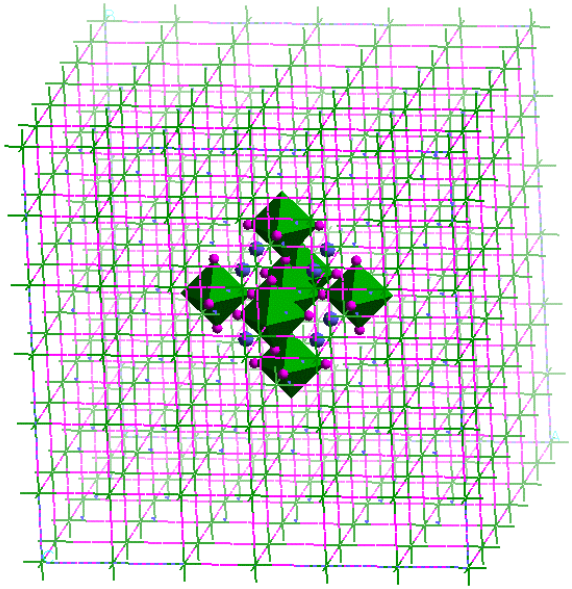
- complement expt; atomic-scale probe; predictive value

Computational Methods

- ***Atomistic***

-Potentials; energy minimisation (>10,000 ions)

-Relaxation around defect



- ***QM/Ab initio***

-DFT framework

-Exchange-correlation: GGA

-Plane-wave + pseudopotentials

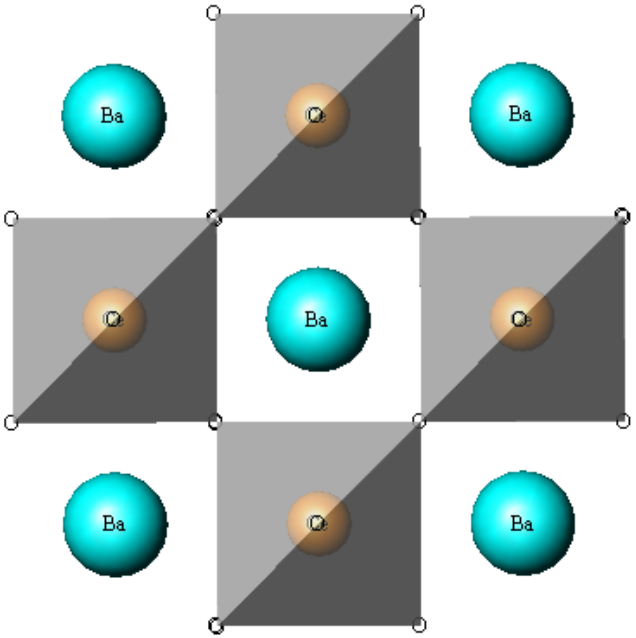
- Previous QM/MD work: Munch/Kreuer

Case Study #1

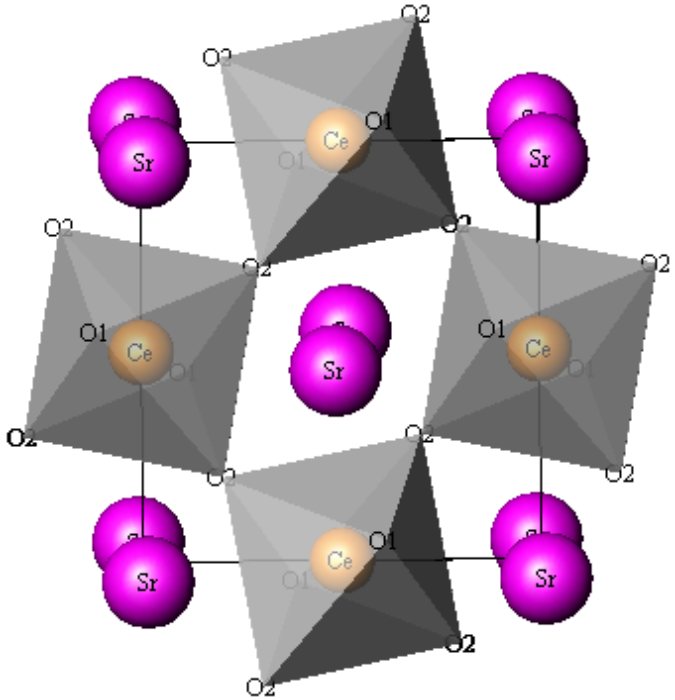
Dopant Sites & Proton Transport

Crystal Structures

Cubic $BaZrO_3$



Orthorhombic $SrCeO_3$



ABO_3: Structural Modelling

- **Potentials & DFT**

			Calc/Å	*Expt/Å*
• $BaZrO_3$	cubic	a	4.188	4.199
• $CaZrO_3$	ortho	a	5.589	5.591
		b	8.055	8.017
		c	5.766	5.761

ΔBond lengths & M-O-M angles < 1.5%

Observed structures reproduced

$CaZrO_3$: Dopants

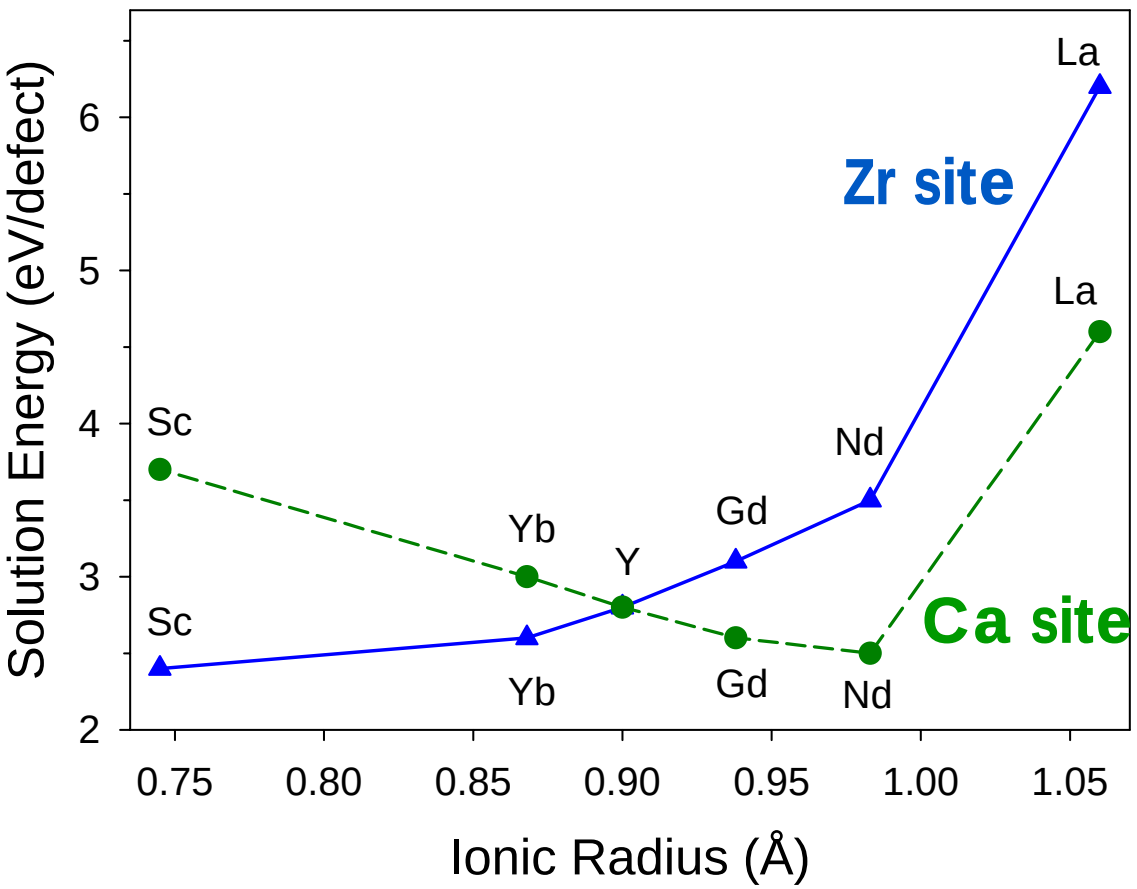
- **Certain dopants (e.g. Nd^{3+}) - low conductivity**

- **Substitution site?**

Dopant $\left\{ \begin{array}{l} Ln'_{Zr} \rightarrow V_O^{\bullet\bullet} \\ Ln^{\bullet}_{Ca} \rightarrow V''_{Ca} \end{array} \right\}$ **Compensating defect**

$$H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^x \rightarrow 2OH_O^{\bullet}$$

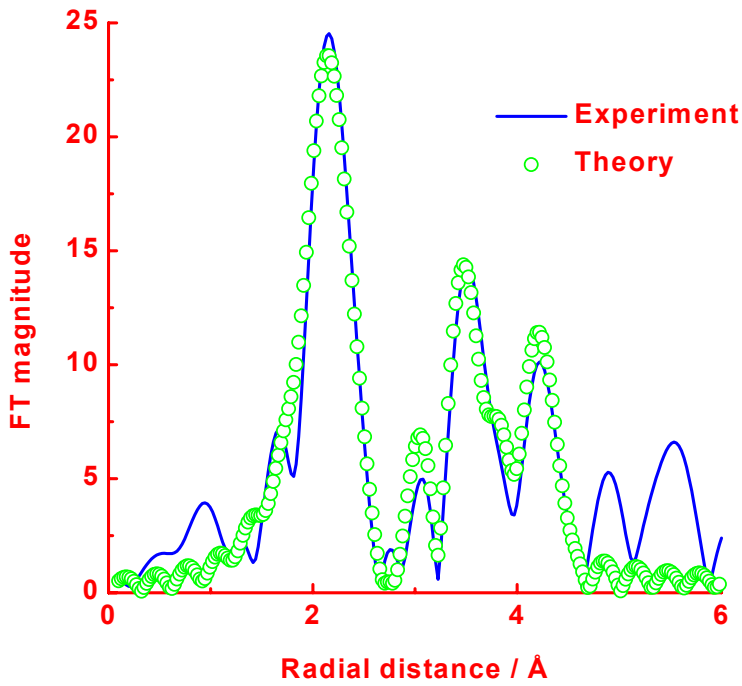
$CaZrO_3$: Dopant Site-Selectivity?



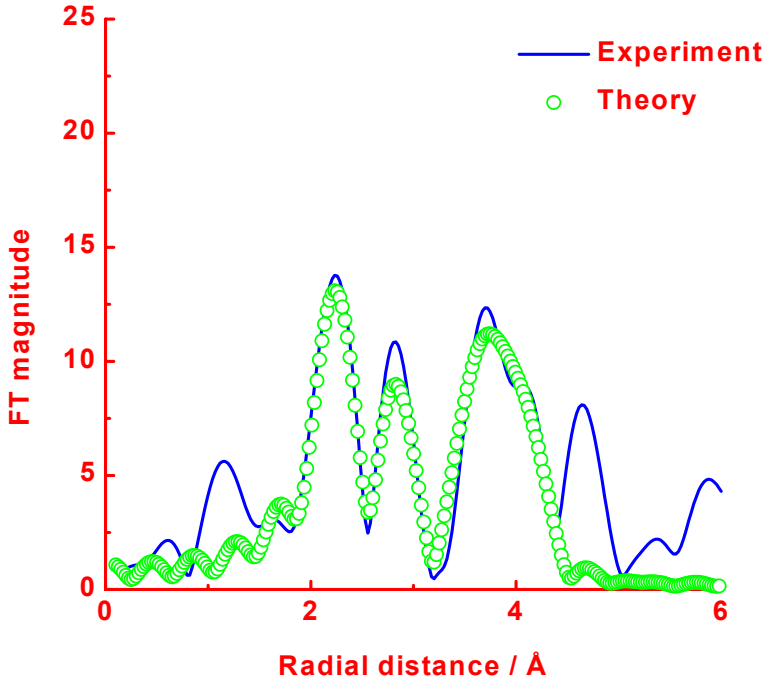
- **Small dopants (*e.g.* Yb^{3+}) Zr-site → $V_O^{\bullet\bullet}$**
- **Large dopants (*e.g.* Nd^{3+}) Ca-site → $V_{Ca}^{''}$**
- **EXAFS evidence**
- **Amphoteric? Y^{3+}**

EXAFS: Yb or Nd doped $CaZrO_3$

Yb --> Zr site

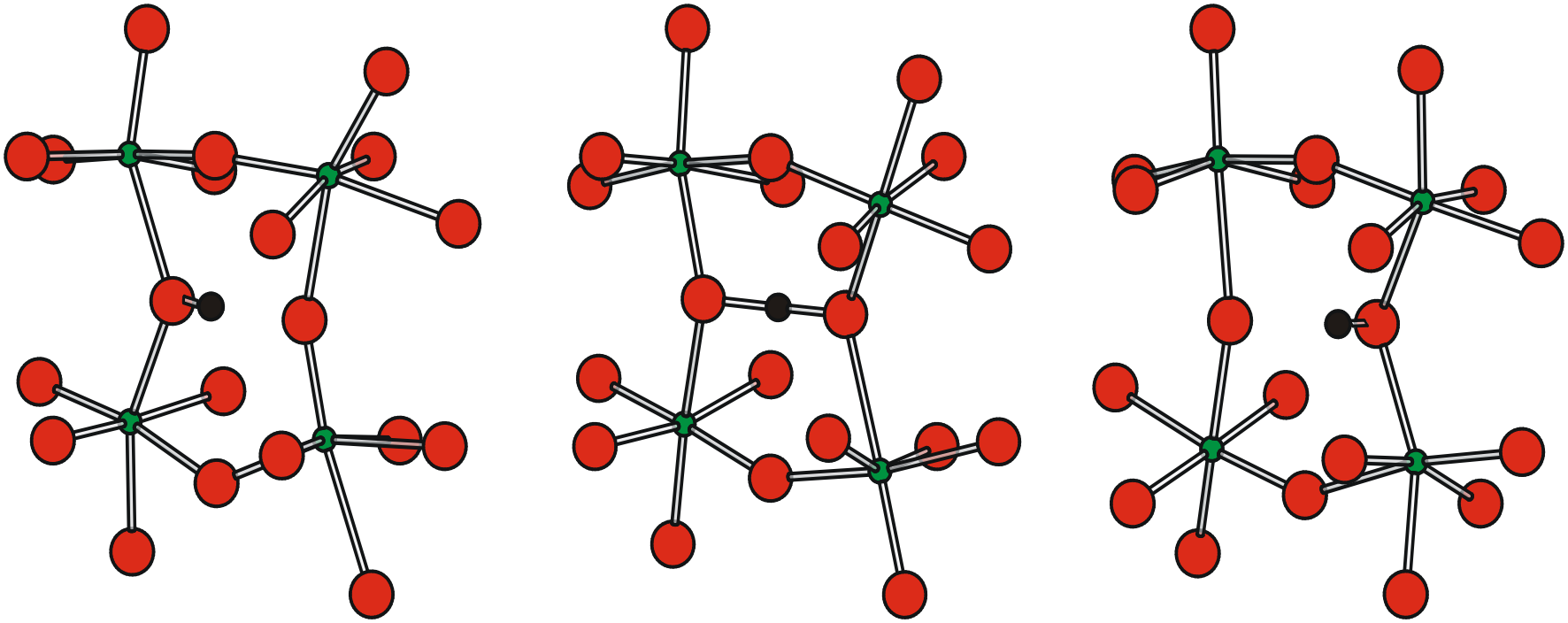


Nd --> Ca site



- **Site-selectivity & local structure** ***(Solid State Ionics, 2000)***

$CaZrO_3$: Proton Transport



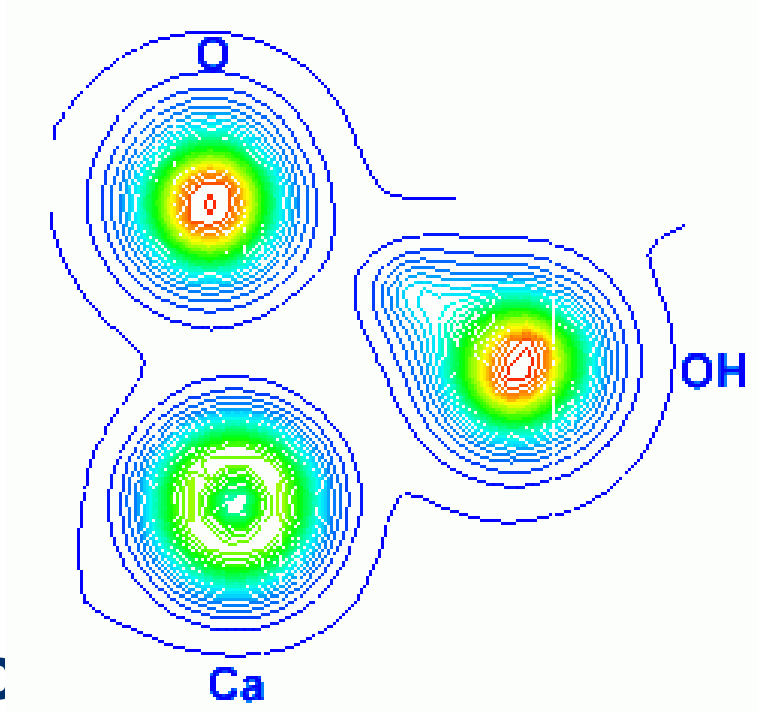
- **Transfer of lone proton (Grötthuss mechanism)**
- **Inter-octahedra hopping**
- **Lattice dynamics; O-O shortens (*ca*. 2.8 to 2.4Å)**

$CaZrO_3$: Migration Energies

- **Energy profiles**

O(1)-O(1) inter-oct ***0.52eV***
O(1)-O(2) intra-oct ***0.74eV***

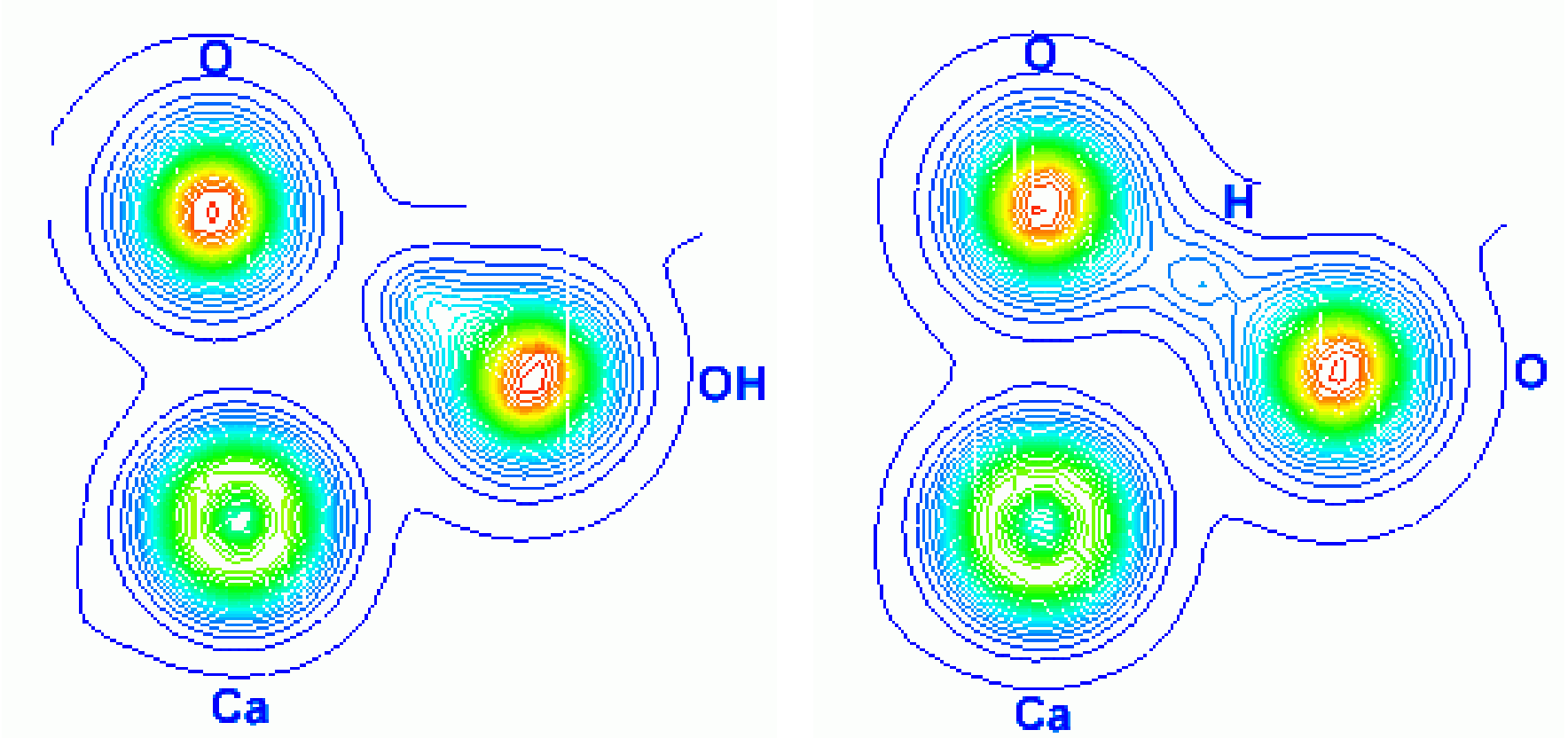
Expt: > 0.7eV ***(Iwahara)***



- **Orthorhombic versus cubic**

(Chem. Mater ,2000)

$CaZrO_3$: Proton Migration

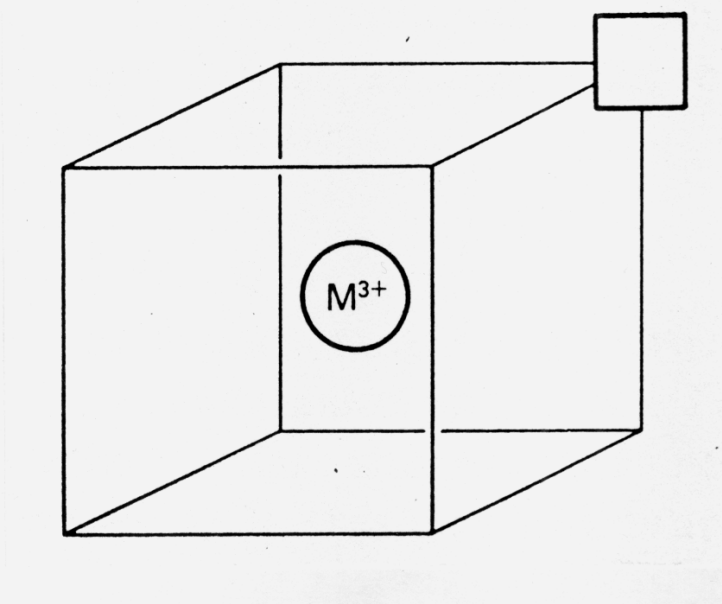


- **Transition state: not “free” proton**
- **Localised spherical-like density: “ionic” character**
  (Chem Comm, 2001)

Case Study #2

Proton-Dopant Interaction?

Defect Association: Fatal Attraction!



Doped CeO_2

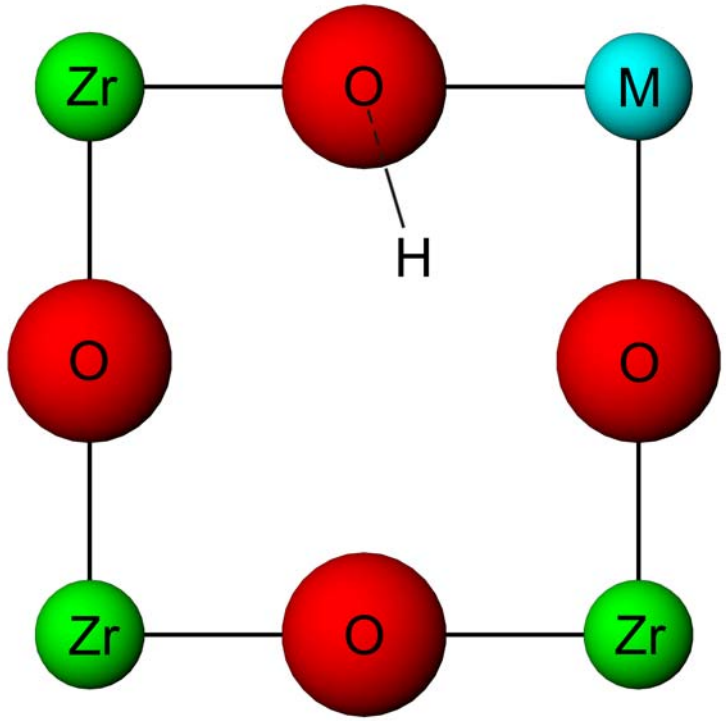
- **Pair Defect Cluster**
- **Binding energy term**

(e.g. Nowick, Kilner, Catlow)

Doped $KTaO_3$; $LaGaO_3$

(e.g. Nowick, Islam, Norby)

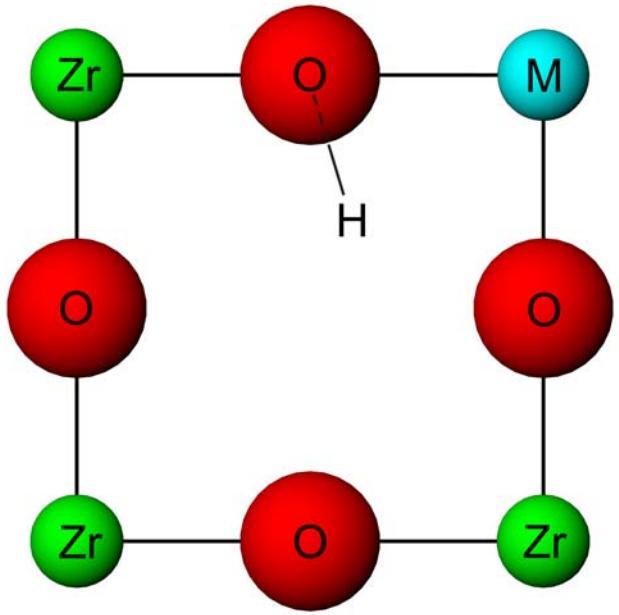
$BaZrO_3$: Dopant-Proton Association?



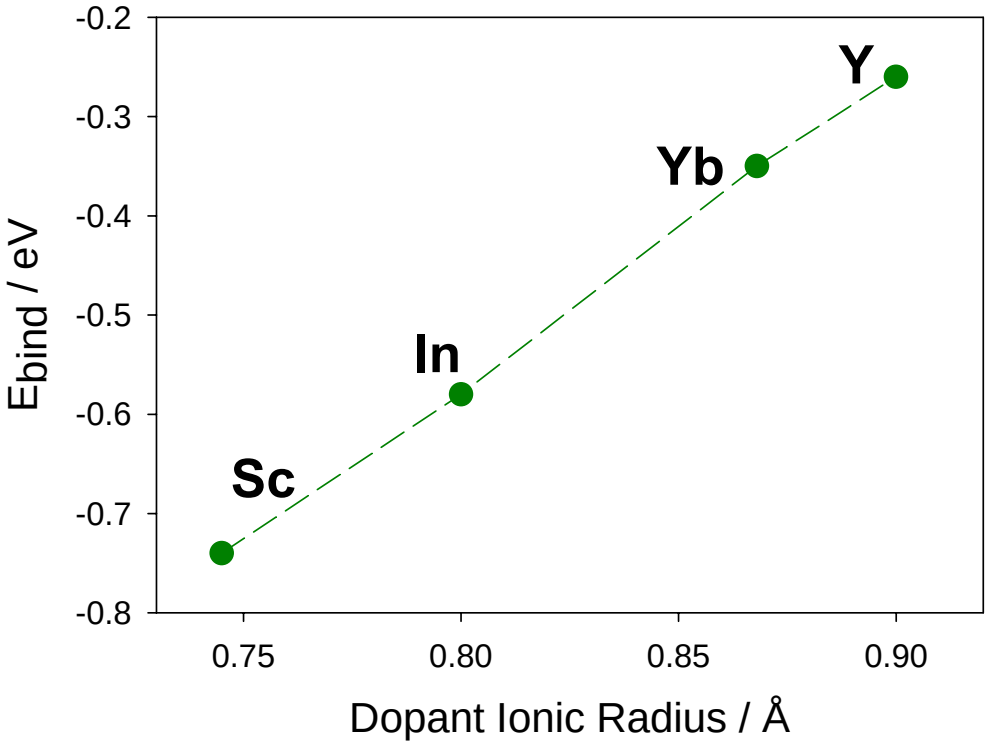
$$E_{\text{bind}} = E_{\text{cluster}} - \left(\sum_{component} E_{\text{isolated defect}} \right)$$

- **muonSR: "trapping" energies: -0.2 to -0.4 eV ($Sc/SrZrO_3$)**
- **Dopant levels: 10-20 %**

$BaZrO_3$: M-OH Binding Energies

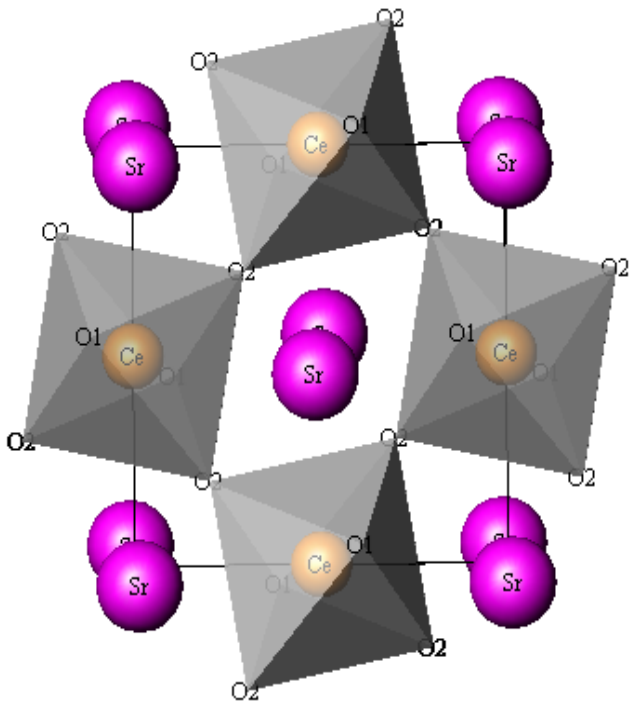


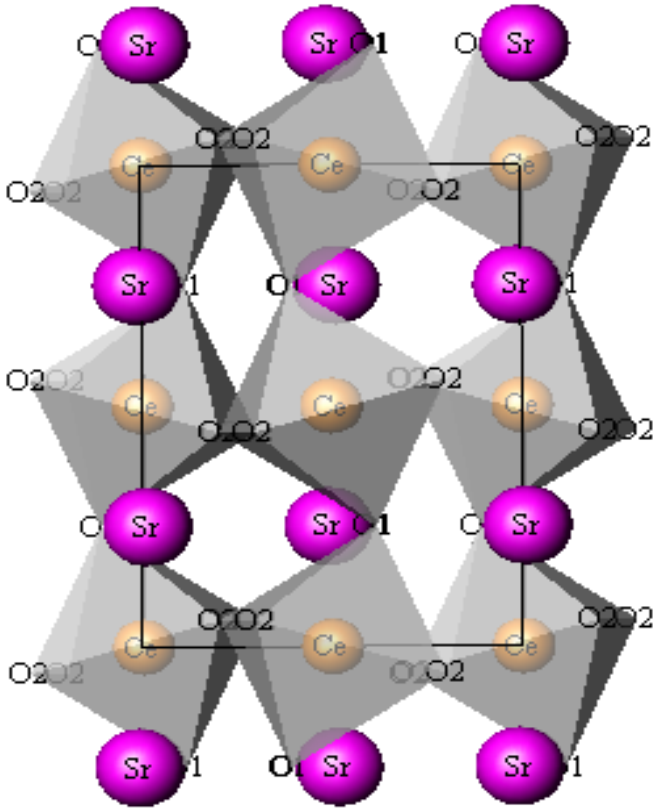
(Dalton Trans, 2004)



- **Predict OH-dopant association: Y << Sc**
- **High proton mobility & conductivity (e.g. Kreuer, 2001)**
  Y > Gd > In > Sc

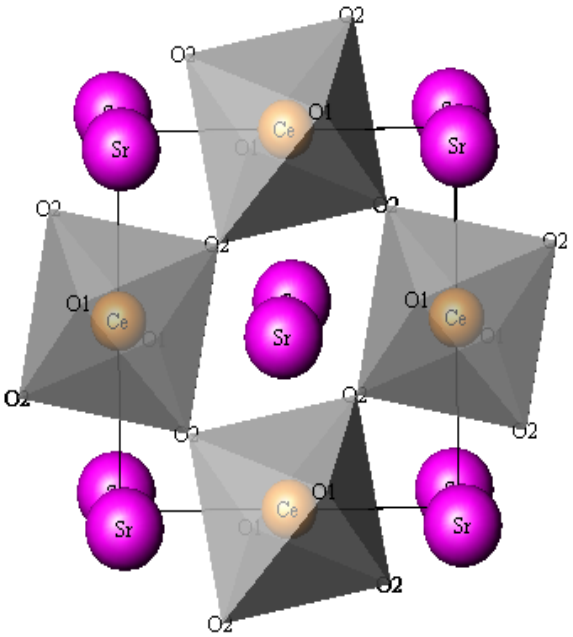
$SrCeO_3$: Distorted Structure

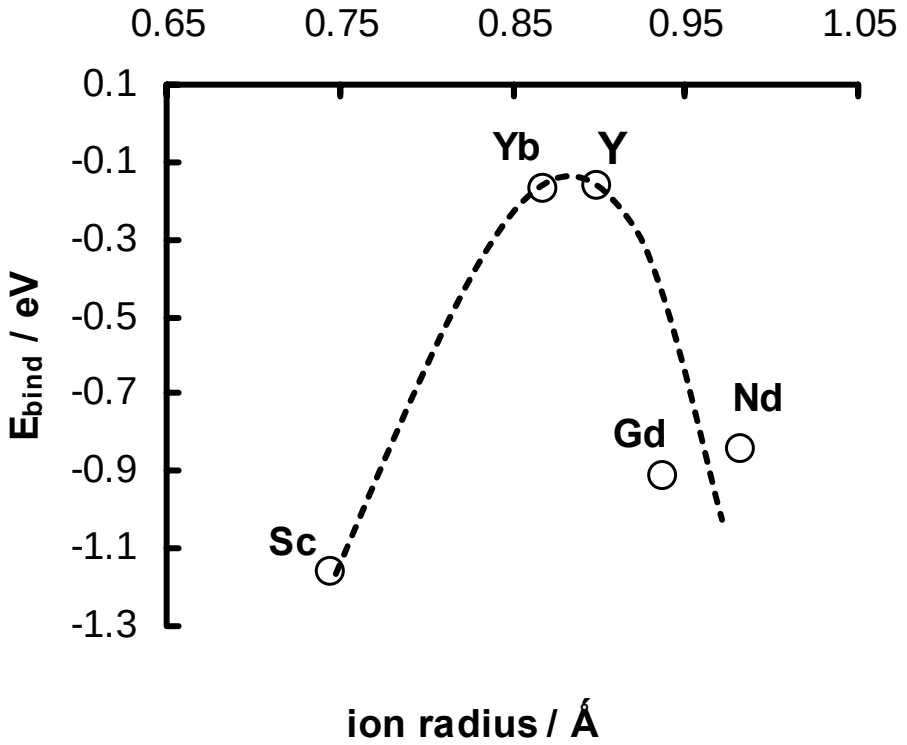




Tilting CeO_6 octahedra

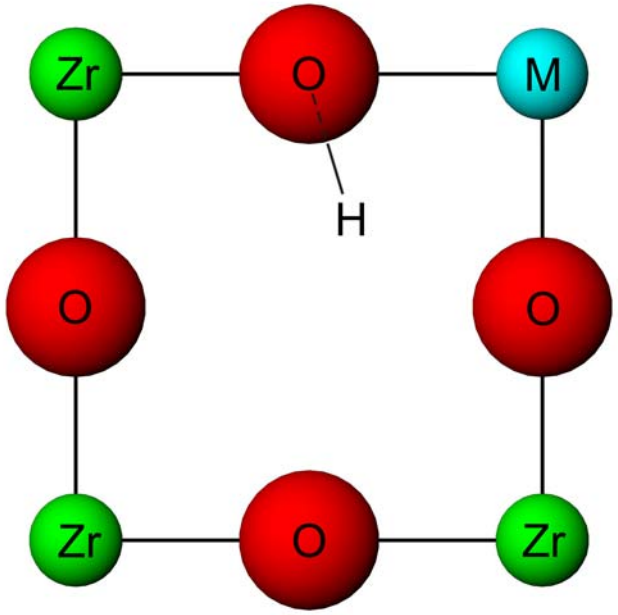
$SrCeO_3$: M-OH Binding Energies



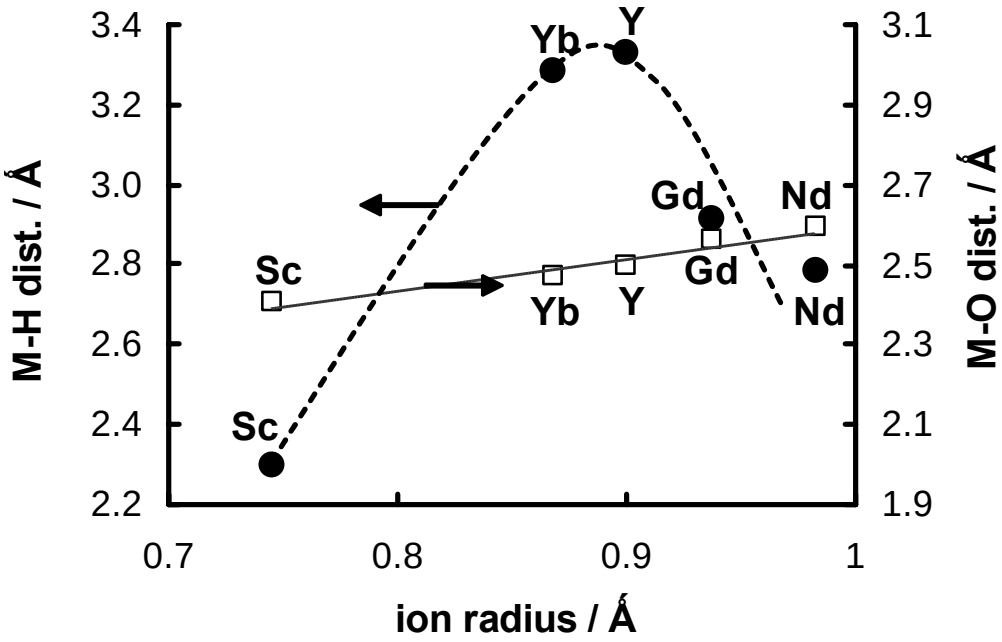


- **Minimum association: Y, Yb**
- **High mobility & conductivity (e.g. Mather, 2004)**
  Y , Yb > Gd, Sc

$SrCeO_3$: Distances of M-OH Cluster



(Chem. Mater., 2005)



M-O dist: very small change

M-H dist: strong variation – same as binding energy

Case Study #3

Non-stoichiometry & oxygen migration

ABO_3: Non-stoichiometry

- **A/B ratio $\neq 1$**

- **Shown to influence**
- dopant behaviour; sintering; chemical stability

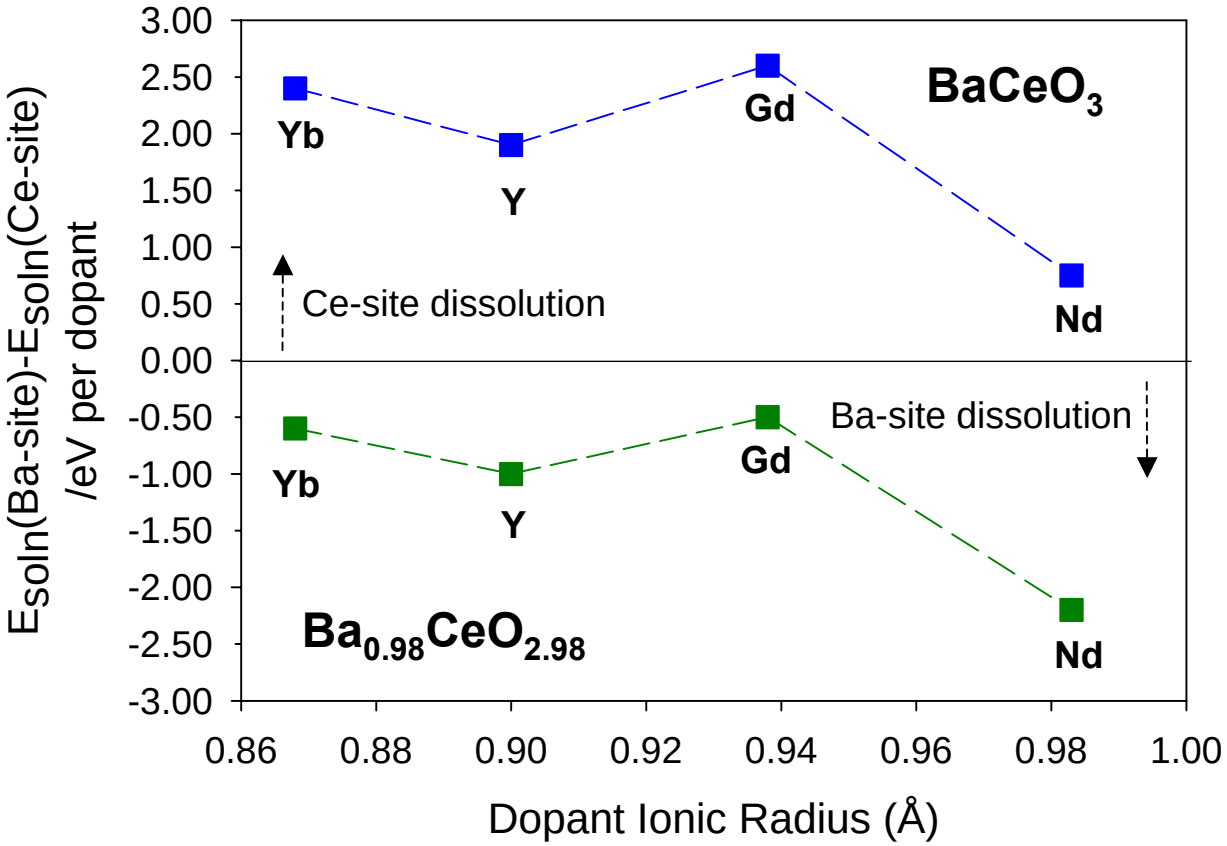
- **$BaCeO_3$: On BaO loss - dopants on "wrong" Ba site**

$\rightarrow$ Reduces proton uptake & conductivity (Haile, 2001)

Barium Cerate: Ba Deficiency

- **Atomistic simulations**
- **Dopants in $BaCeO_3$ & $Ba_{0.98}CeO_{2.98}$ (supercell)**
- ***ΔE = Esol (Ba site) - Esol (Ce site)***
- **Positive value $\rightarrow$ Ce site occupancy**

Ba Deficiency: Dopant Site-Selectivity



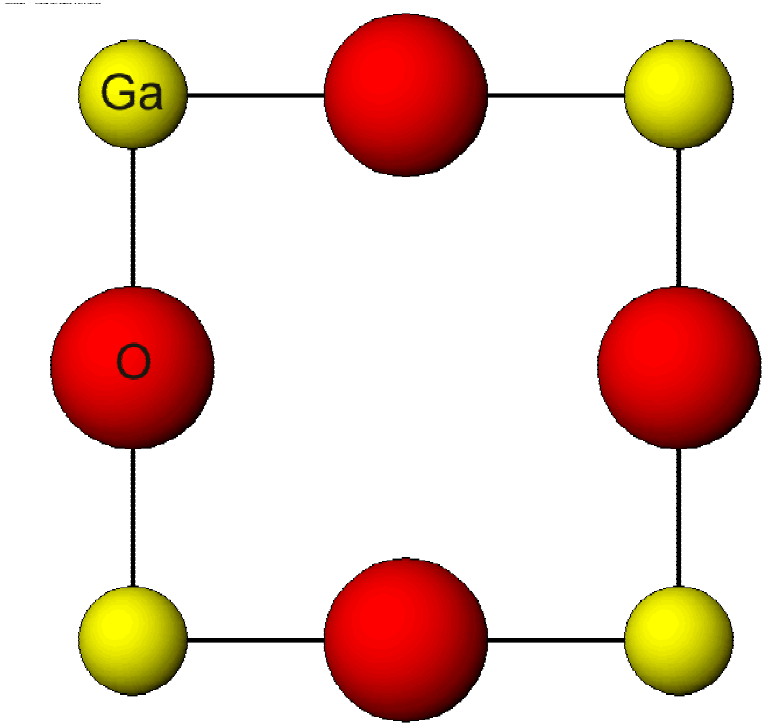
- **Stoichiometric: Yb, Y, Gd on Ce**
- **Ba-deficient: Strong shift to Ba site**
- **Nd dopant: partitioning over both sites ("amphoteric")**
- **Reduce O vacancy concn --> lower conductivity**

Oxide ion migration: $ACeO_3$

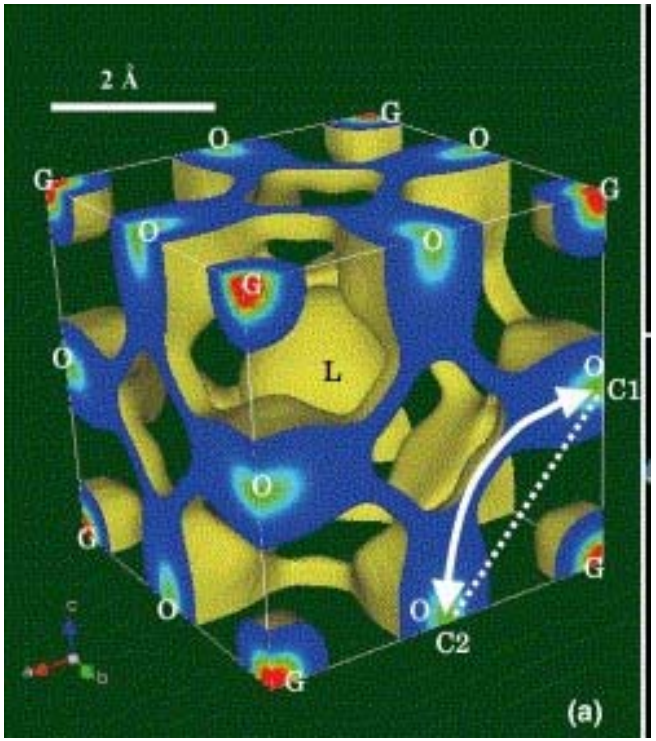
- **Proton conductivity: $SrCeO_3 < BaCeO_3$**
- **Oxide ion cond: Sr > Ba**
- **Y or Yb doped $SrCeO_3$:**
- **Sensor & membrane applications *(Iwahara)***

Oxide ion migration: $ACeO_3$

- **$SrCeO_3$: 0.7eV; $BaCeO_3$: 0.9eV**
- **Curved path**



J. Mater Chem, 2000; Chem. Mater, 2005



Yashima et al (2003)

Oxide ion migration: $ACeO_3$

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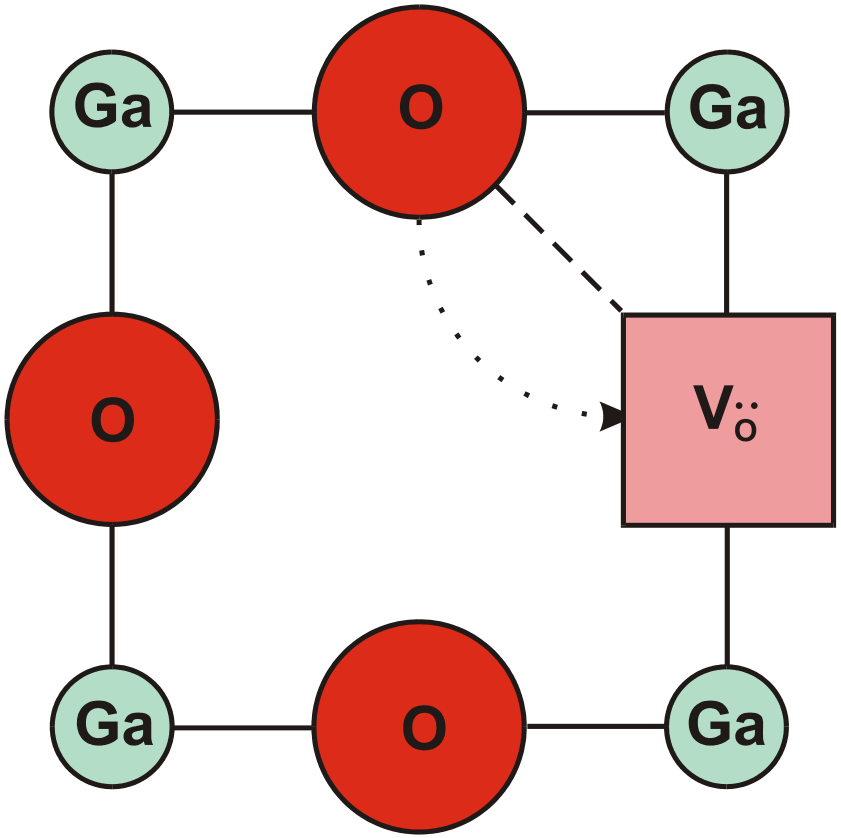

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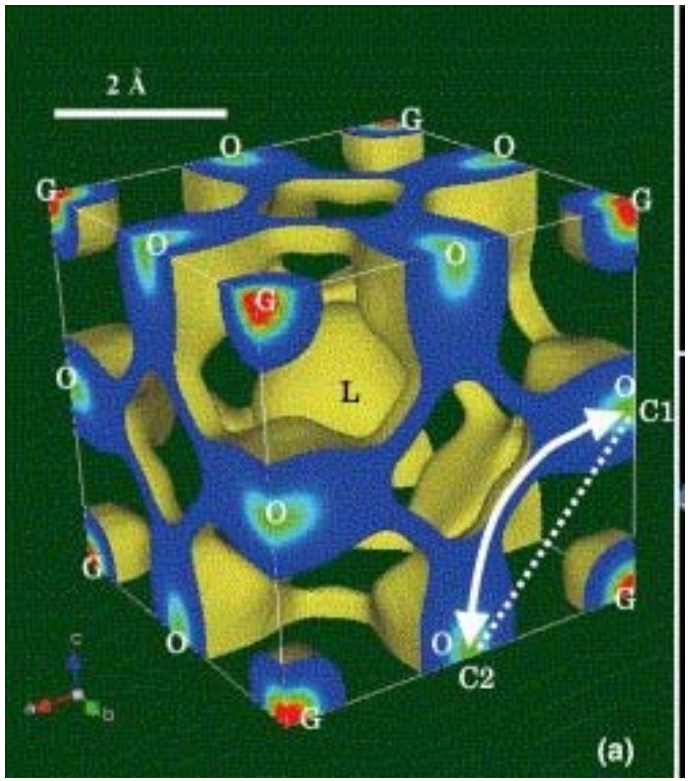


Yashima et al (2003)

Summary

Summary

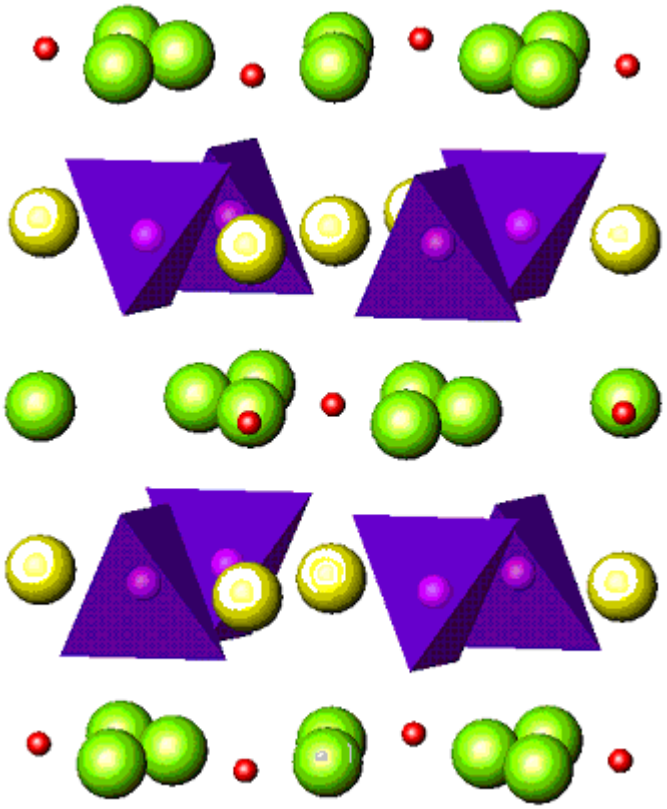
• Probed structure-composition-property relationships of complex oxides

- *modelling on atomic-scale with strong experimental links*

-Proton migration
-Dopant sites & non-stoichiometry
-Dopant-OH association “proton trapping”
-Oxide ion migration

Current Work

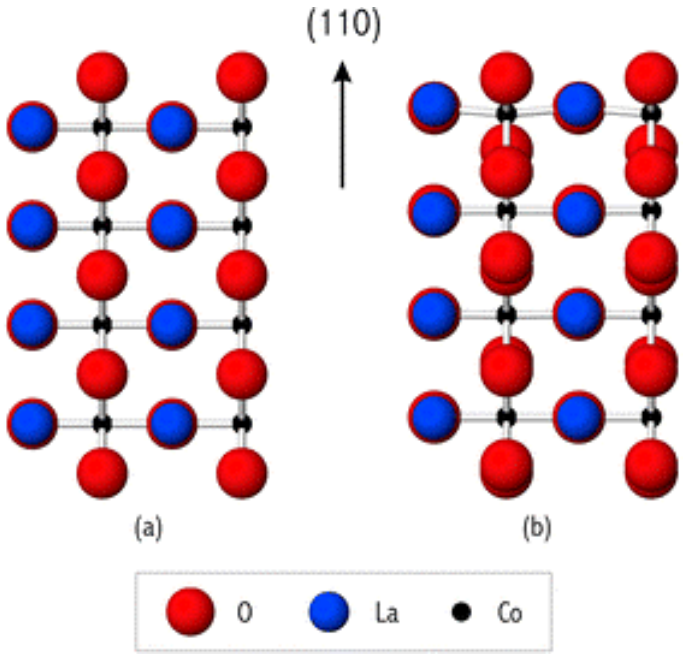
- **Challenge: breakthrough research to find new materials**
- **Basic science that 'underpins' applied work**
- **New $LaBaGaO_4$ based proton conductor**



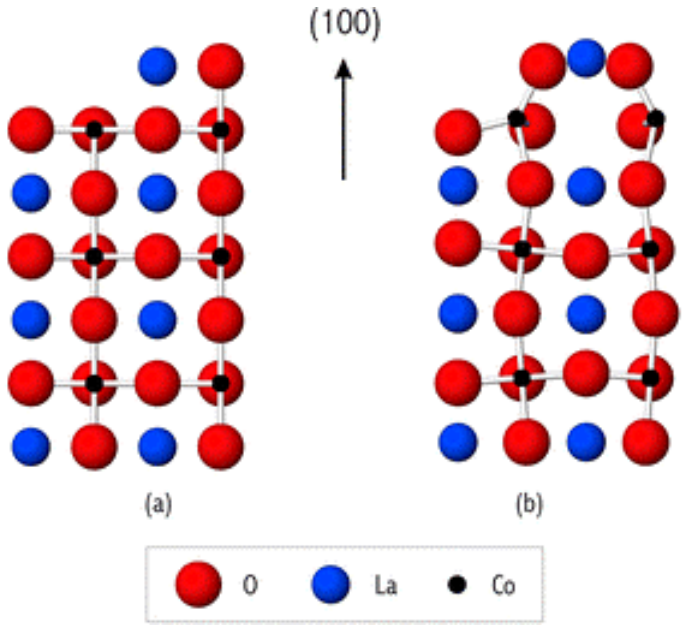
P.Slater, Chem. Comm., 2003

Current Work: Surface Structures

- **$LaCoO_3$: Relaxation- not bulk termination**



O termination

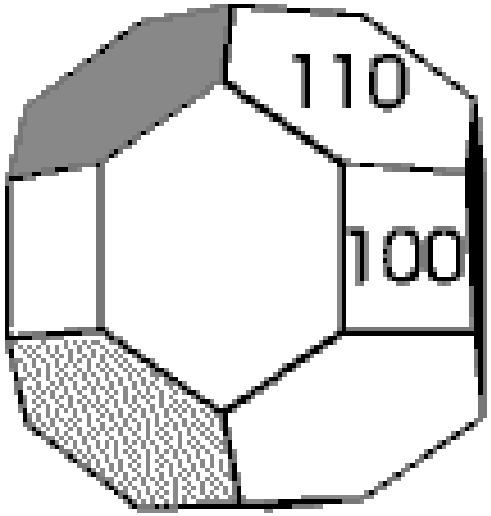


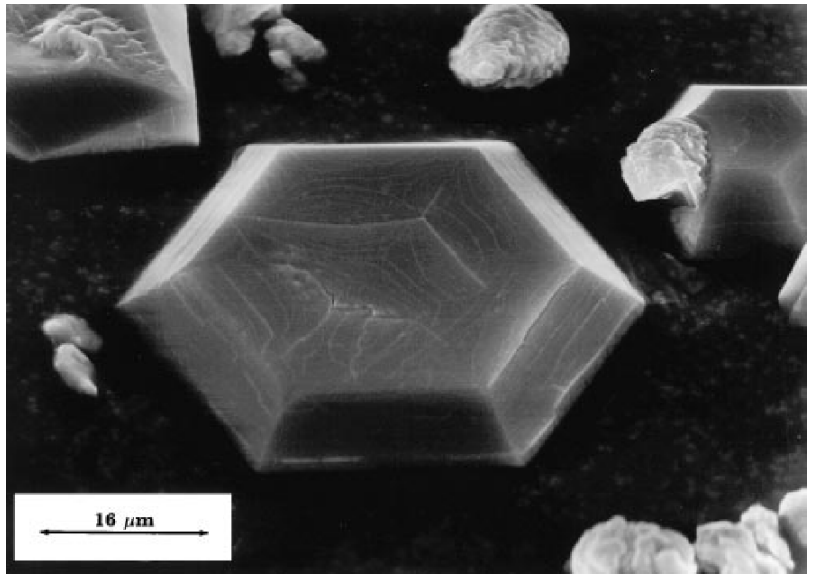
La/O termination

- **Consistent with Low Energy Ion Scattering of $SmCoO_3$**

Crystal morphology: $LaCoO_3$

- **Calc: hexagonal-like habit** ***(Solid State Ionics, 2002)***





Current work – influence of OH groups on surfaces & morphology

Consistent with SEM of $LaFeO_3$ (Traversa et al)

Acknowledgements

- **Surrey: P.R. Slater**
  Postdocs: R.A. Davies; C. Fisher; E. Kendrick

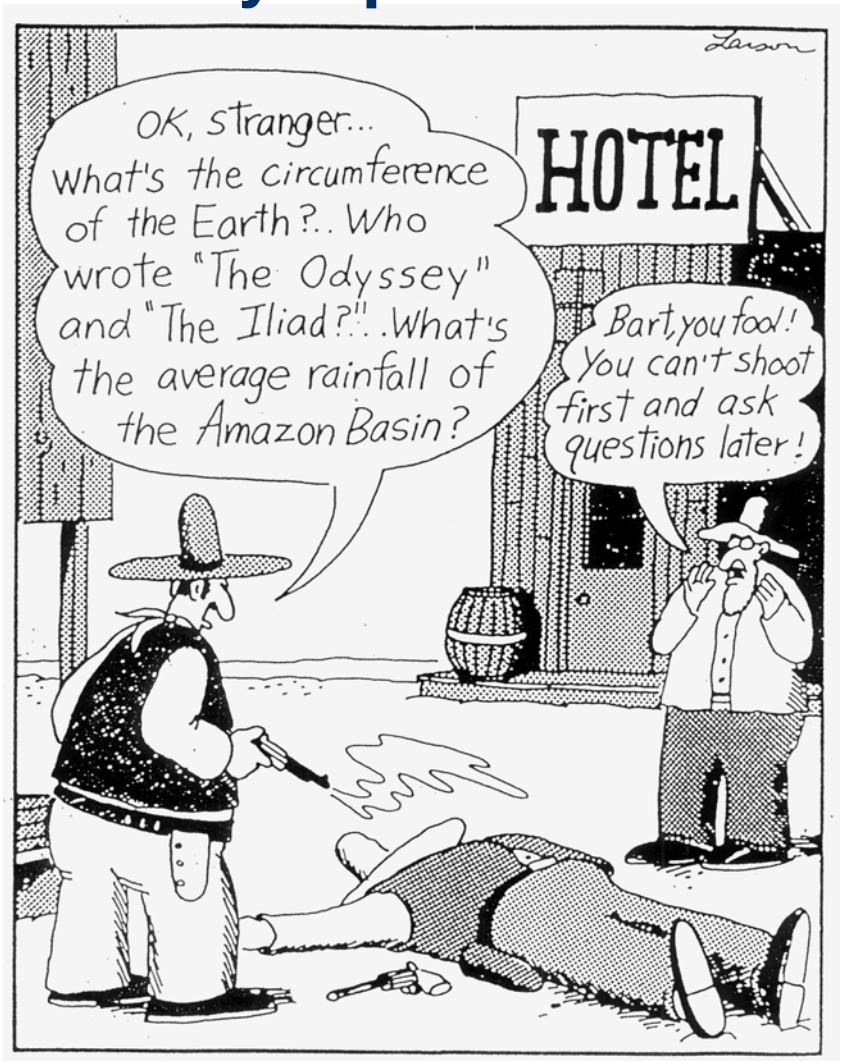
- **J. Gale (Perth, Aus)**
  A. Chadwick (Kent)
  S. Haile (Caltech,US)
  G. Mather (Madrid, Sp)

- **EPSRC**
- **Leverhulme Trust**

Conference Alert!

- **RSC Faraday Discussion (FD134) Meeting**
- **Atomic Transport & Defect Phenomena in Solids**
- ***10-12 July 2006, Univ of Surrey, UK***

Finally…questions??



The End

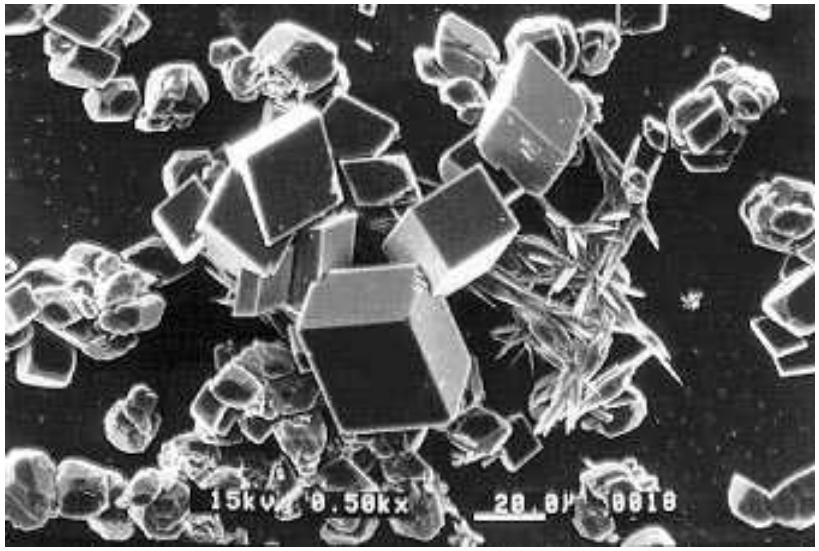
Main Results

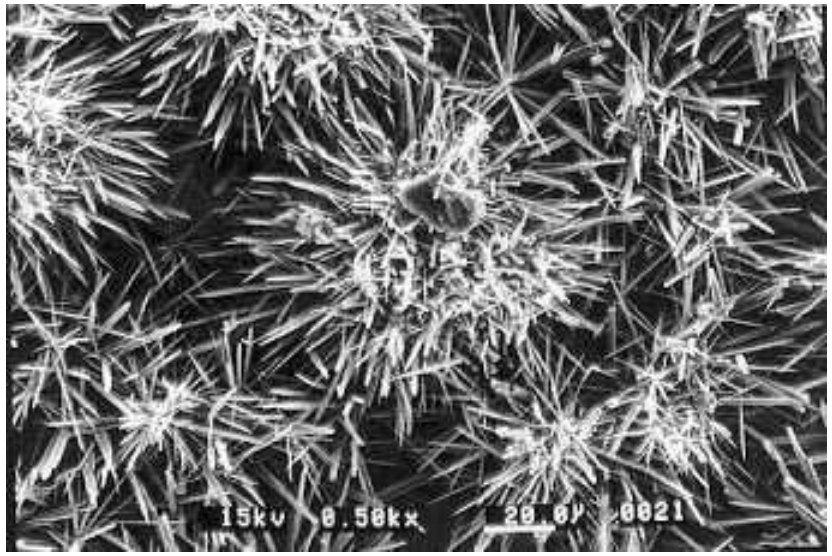
- **$CaZrO_3$:**
  Dopant sites; proton migration mechanism

- **BaZrO3 & SrCeO3:**
  Dopant-OH association: proton 'trapping'

- **LaScO3:**
  Oxide ion migration; surfaces & morphology

“Crystal Gazing”: Morphology



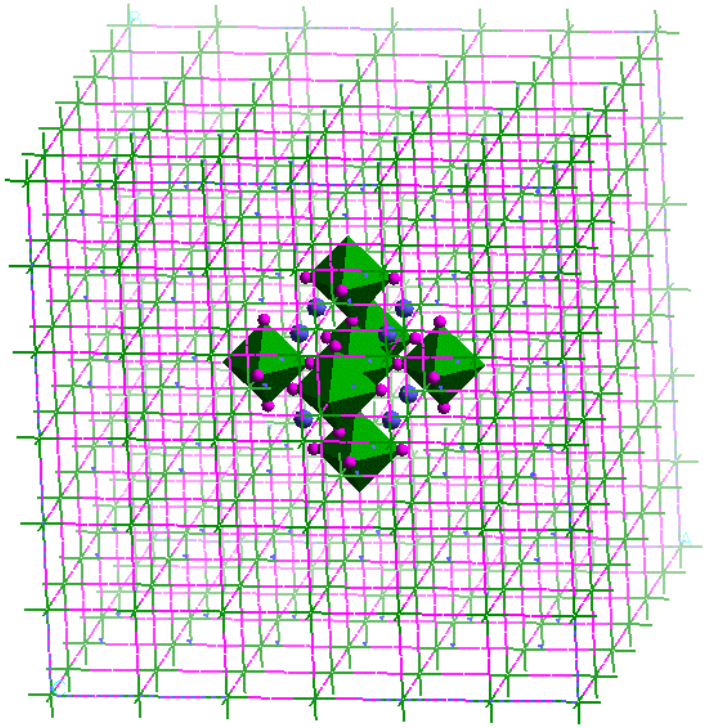


Atomistic Simulation

- **Born Model**
  - **Buckingham potential**

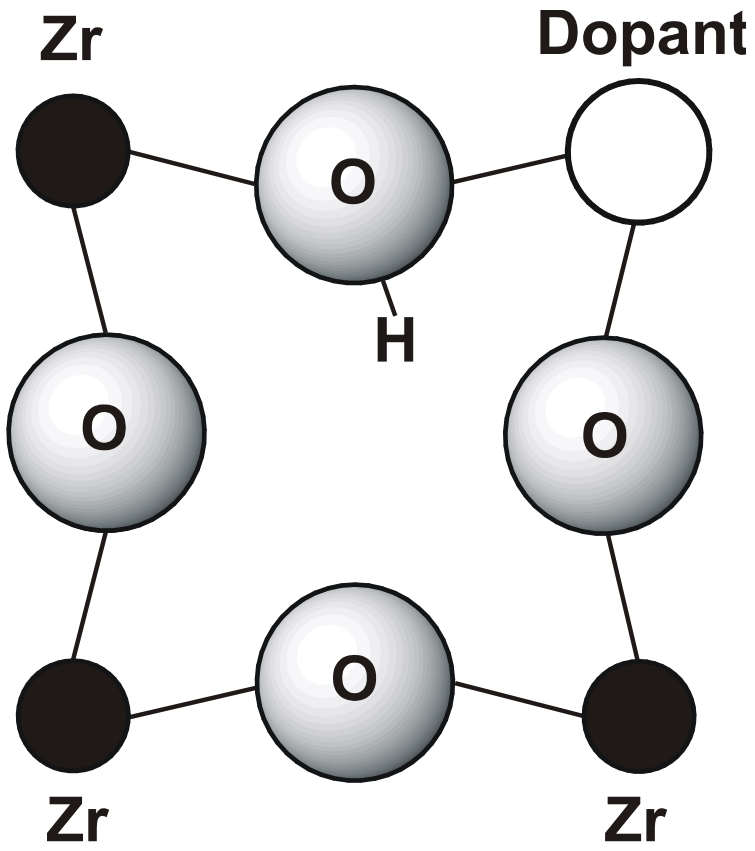
$$U(r) = \left[-\frac{q_i q_j}{r_{ij}} \right] + \sum_{ij} A \exp(-r_{ij} / \rho_{ij}) - C / r_{ij}^{6}$$

- **Ionic polarisation**
- **Energy minimisation (> 10,000 ions)**
- **Mott-Littleton relaxation around defect**



DOPANT-PROTON ASSOCIATION?

Dopant	E_{bind} / eV
Ga^{3+}	-0.18
Sc^{3+}	-0.31
In^{3+}	-0.30



- Favourable binding energies - predict OH-dopant pairs
- μSR: "trapping" energies

-0.2 to -0.4 eV (Sc doped $SrZrO_3$)

$LaMO_3$: Dopant-Defect Clusters

Dopant	*$LaGaO_3$*	*$LaScO_3$*
Sr^{2+} on La	0.00	-0.22
Ca^{2+} on La	-0.08	-0.27
Mg^{2+} on M	-0.90	-0.63
In^{3+} on M	-0.45	0.03

- Greater "trapping" in $LaScO_3$ → higher Eact
- Isovalent (In) → elastic strain effects
- Expt: should include binding terms

$BaCeO_3$: Acceptor Dopants

(i) $2Ce_{Ce}^{x} + O_o^{x} + M_2O_3 \rightarrow 2\,M'_{Ce} + V^{\bullet\bullet}_o + 2CeO_2$

(ii) $H_2O + V^{\bullet\bullet}_o + O_o^{x} \rightarrow 2OH_o^{\bullet}$

- **H_2O uptake & proton conductivity:**
  Yb > Gd >> Nd

- ***Haile (2001):***
  Dopants on "wrong" Ba site (on BaO loss)

$\rightarrow$ Reduces O vacancy concn

- YASMIN
- ZAK
- MUMMY
- DADDY