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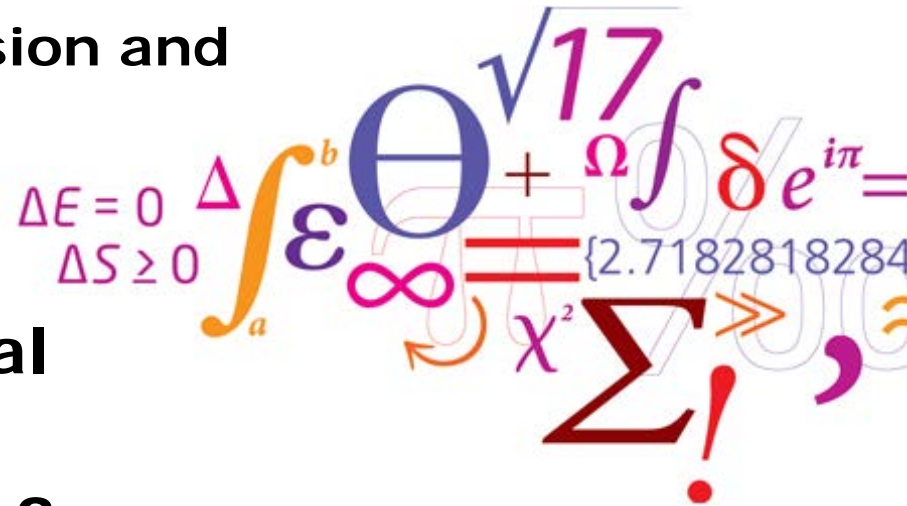
# Volume of Oxide Vacancies in Fluorite and Perovskite Structured Oxides

Mogens B. Mogensen, Poul Norby,  
Christodoulos Chatzichristodoulou, Peter V.  
Hendriksen

Department of Energy Conversion and  
Storage

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# Introduction

**Even though I never got to know Prof. Nowick, I know that some of his deep interests were properties of fast ion conductors and defect chemistry in general**

**I also know that he was Harry Tuller's PhD supervisor. Apart from all Prof. Nowick's own seminal scientific contributions, the contribution of educating Harry was - as time has proven – another great contribution to the science of ionic and mixed ceramic conductors**

**We will in the following minutes discuss about such materials and the volume of defects, i.e. the volume of oxide vacancies, inside them in memory of Prof. Arthur S. Nowick**

# Why is volume of vacancies interesting?

Some reasons are the observations that:

- the crystal lattice shrinks if a fluorite like  $\text{CeO}_2$  is doped with a 2 or 3-valent cation of approximately the same size as  $\text{Ce}^{4+}$
- the induced ionic conductivity reaches its maximum as a function of dopant radius for the radius that does not change the lattice parameter of the host crystalline compound
- or expressed differently: The highest conductivity occur if Vegard's slope is zero
- or the conductivity - for a given dopant concentration - is highest in the stress free lattice

# Lattice constant empirical relations of doped fluorites

Empirical (Kim 1989):

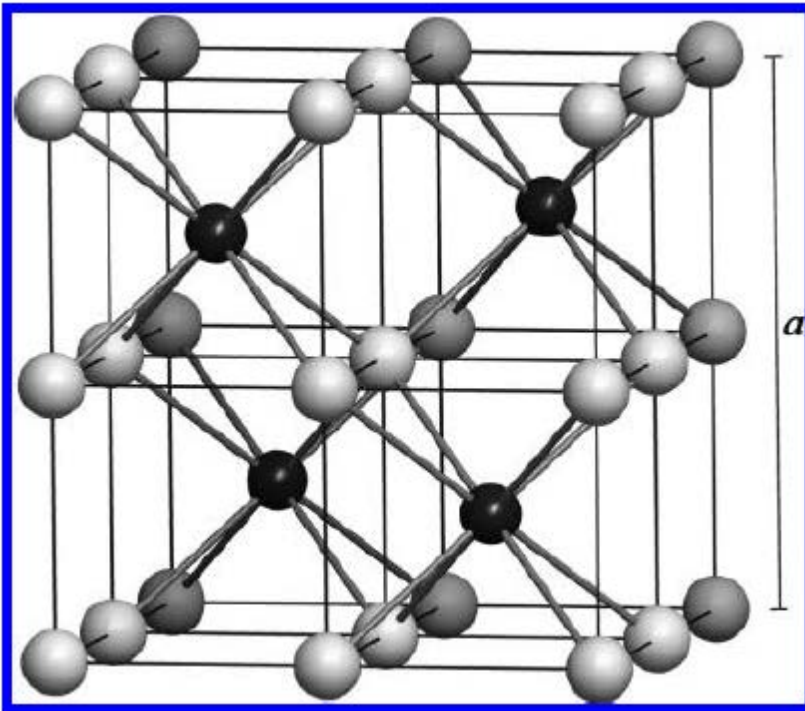
$$a = a_0 + (A \cdot \Delta r_{cat} + B \cdot \Delta z_{cat}) \cdot x$$

Vacancies (Hong and Virkar 1995, Tuller et al 2012):

$$a = \frac{4}{\sqrt{3}} (r_{cat} + r_{an})$$

$$r_{cat} = (1 - x) \cdot r_h + x \cdot r_s$$

$$r_{an} = \left( \frac{2 - x/2}{2} \right) \cdot r_O + \left( \frac{x/2}{2} \right) \cdot r_V$$

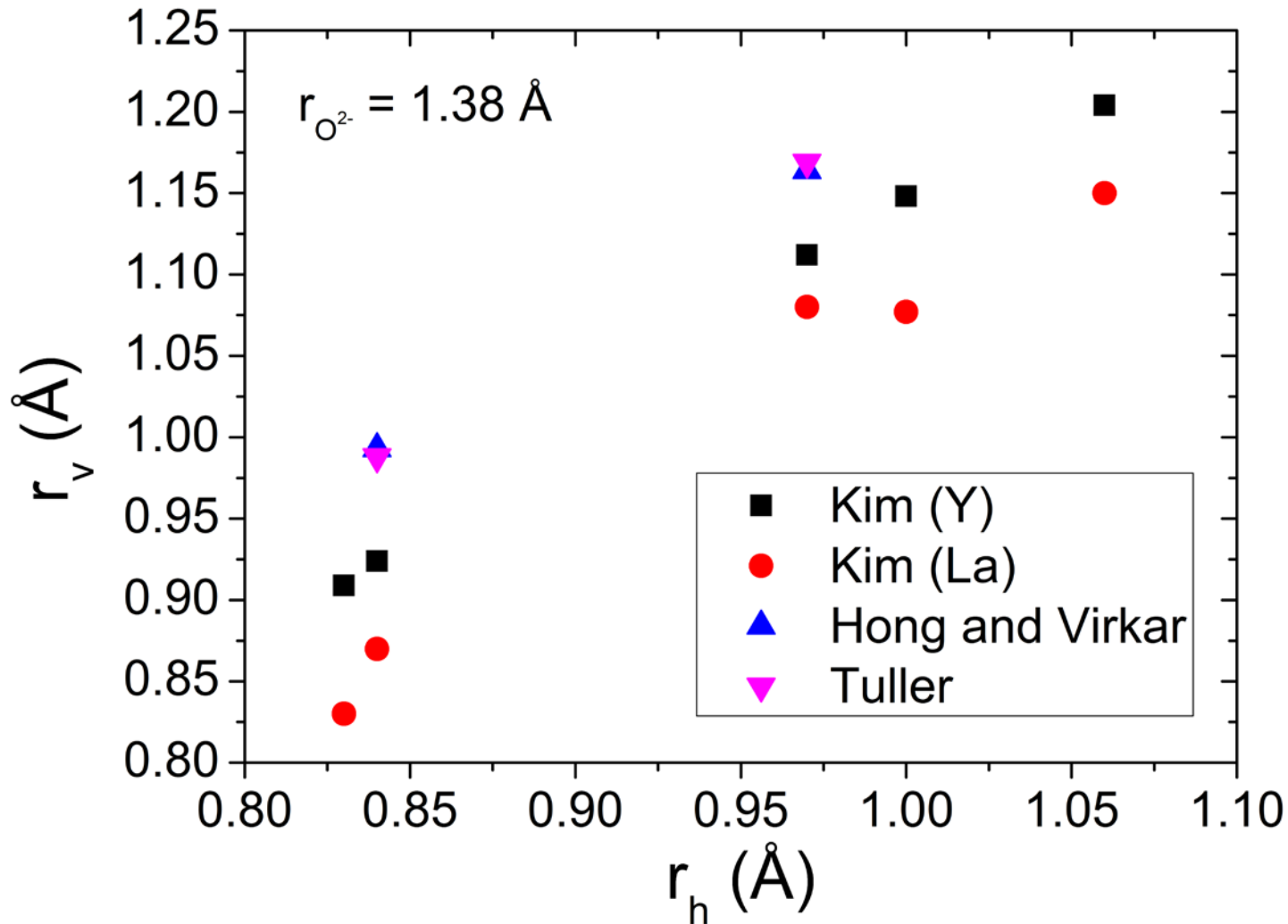


# Estimation of the oxide ion vacancy radius

$r_v$ (Å)					
Compound	Ref.	Kim		Hong+Virkar	Tuller
<b>HfO<sub>2</sub></b>		0.999- 0.484·Δr	0.909 (Y) (0.830 (La))		
<b>ZrO<sub>2</sub></b>		0.982- 0.328·Δr	0.924 (Y) (0.870 (La))	0.993	0.988
<b>CeO<sub>2</sub></b>		1.120- 0.189·Δr	1.112 (Y) 1.080 (La)	1.164	1.169
<b>UO<sub>2</sub></b>		1.155- 0.432·Δr	1.148 (Y) 1.077 (La)		
<b>ThO<sub>2</sub></b>		1.189- 0.328·Δr	1.204 (Y) 1.150 (La)		

$$r_v = r_o - \sqrt{3} \cdot B - (4 - \sqrt{3} \cdot A) \cdot \Delta r_{cat}$$

# Dependence of oxide ion vacancy radius on host size



The weaker metal-oxygen bond the larger is the vacancy volume

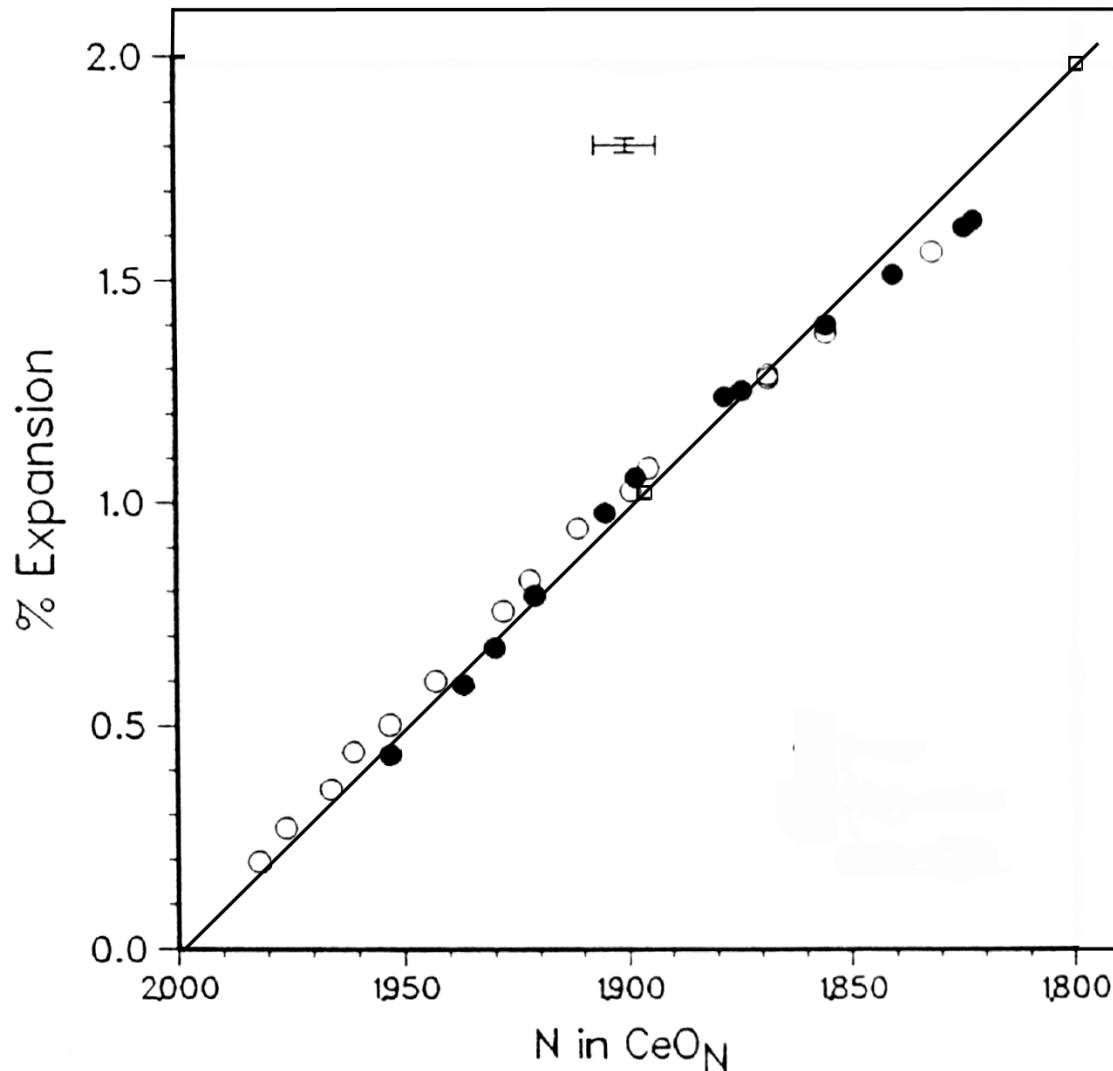
# Estimation of (3+)cation matching radius

$r_c$ (Å)				
system	Ref.	Kim	Hong+Virkar	Tuller
HfO <sub>2</sub>		0.938		
ZrO <sub>2</sub>		0.948	0.937	0.938
CeO <sub>2</sub>		1.038	1.024	1.024
UO <sub>2</sub>		1.063		
ThO <sub>2</sub>		1.112		

$$r_c = r_h + \frac{B}{A}$$



# Expansion on reduction of ceria



Main data: Chiang *et al.* *Solid State Ionics*, **66** (1993) 85–95

Squares: G. Mogensen, M. Mogensen, *Thermochim. Acta*, **214** (1993) 47–50;

Line: best fit: M. Mogensen *et al.*, *Solid State Ionics*, **129** (2000) 63

# Stoichiometry expansion coefficients

Stoichiometry expansion coefficient,  $\alpha_s$ , defined by:

$$\varepsilon = \Delta L/L = \alpha_s \cdot \delta$$

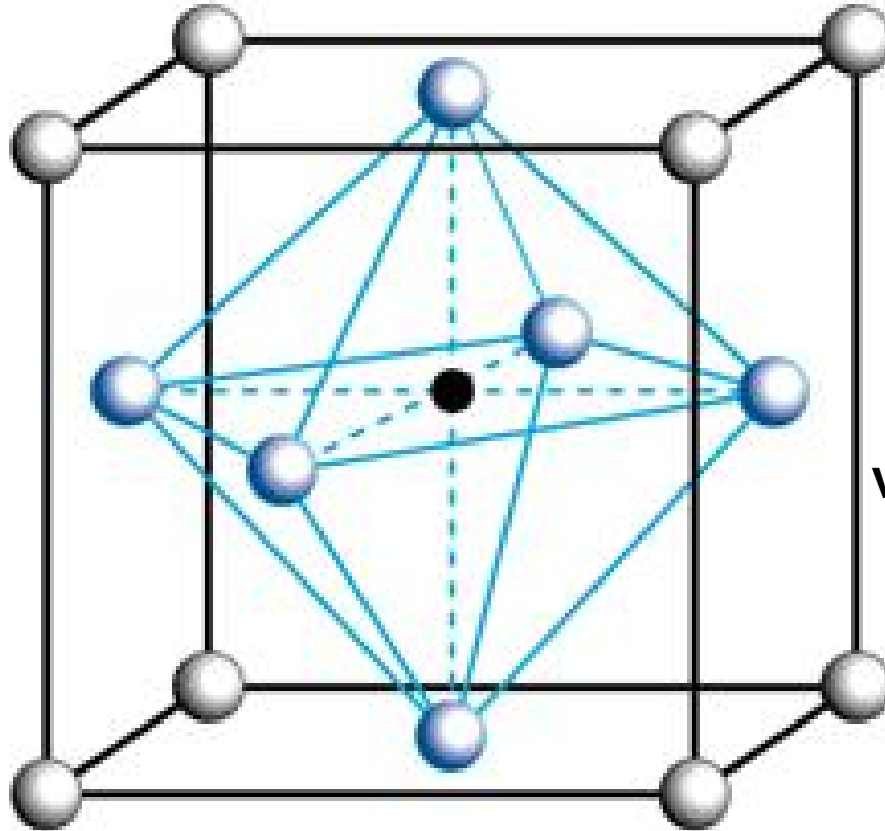
where  $\varepsilon$  is the measured expansion,  $L$  is sample length, and  $\Delta L$  is the change due to a change in oxygen stoichiometry of  $\delta$  e.g. in reduced  $\text{CeO}_{2-\delta}$  or in doped  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ .

P.V. Hendriksen et al., "Electrical conductivity and dimensional stability of co-doped lanthanum chromites", In: *Ionic and mixed conducting ceramics V*; eds. T.A. Ramanarayanan et al. Electrochemical Society Proc. Vol. PV 2004-25, 2008. p. 349-367.

$\alpha_s$  is about in the range of 2.3 – 3 %/vacant O for reduction of various doped  $\text{LaCrO}_3$  and typically about 11 %/vacant O for reduction of ceria

# Perovskite

After V. P. Dravid

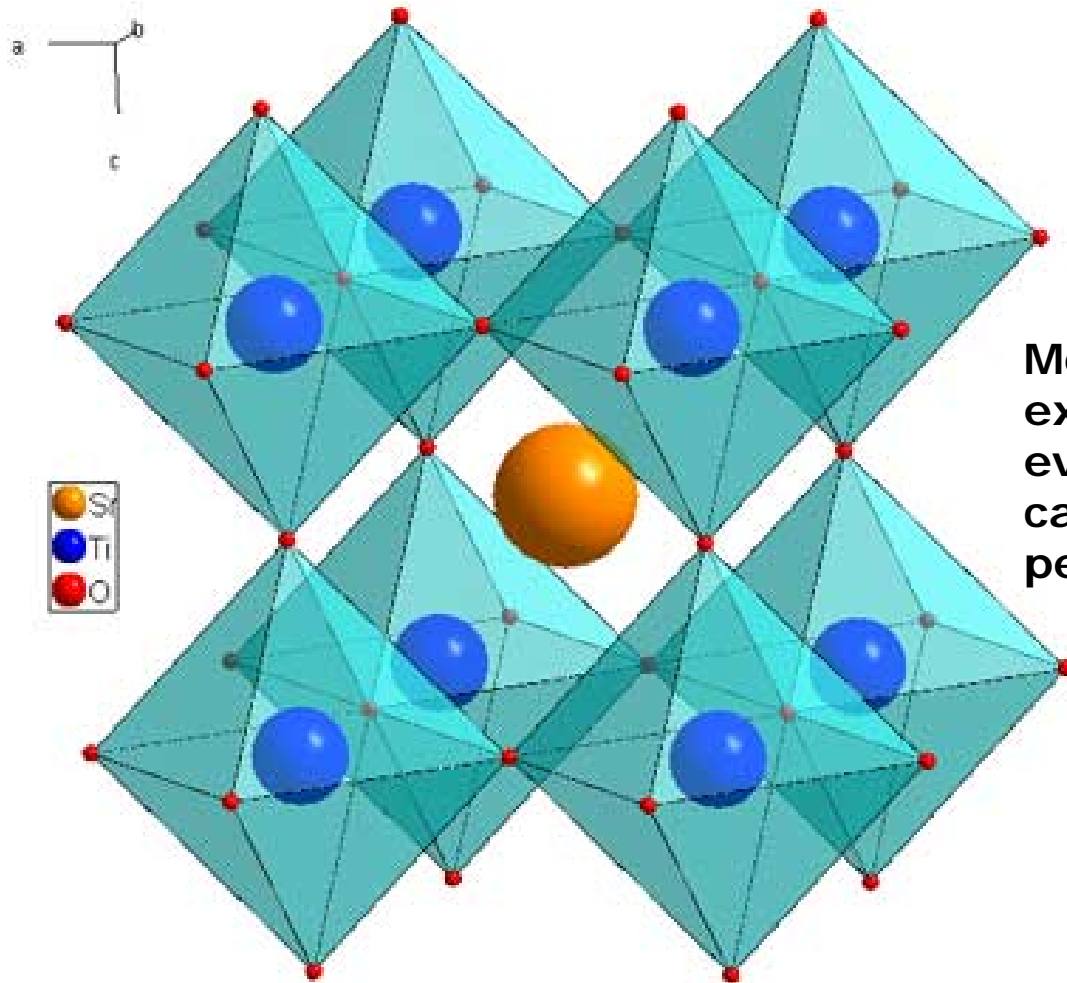


The O + A ions form together a cubic closest packed structure if the size of the A-ion is close to the size of the oxide ion.

Very strong B-metal-oxygen bonds

Perovskite structure (Grey atoms: A, Black: B, Blue: O)

# Perovskite – a very flexible structure

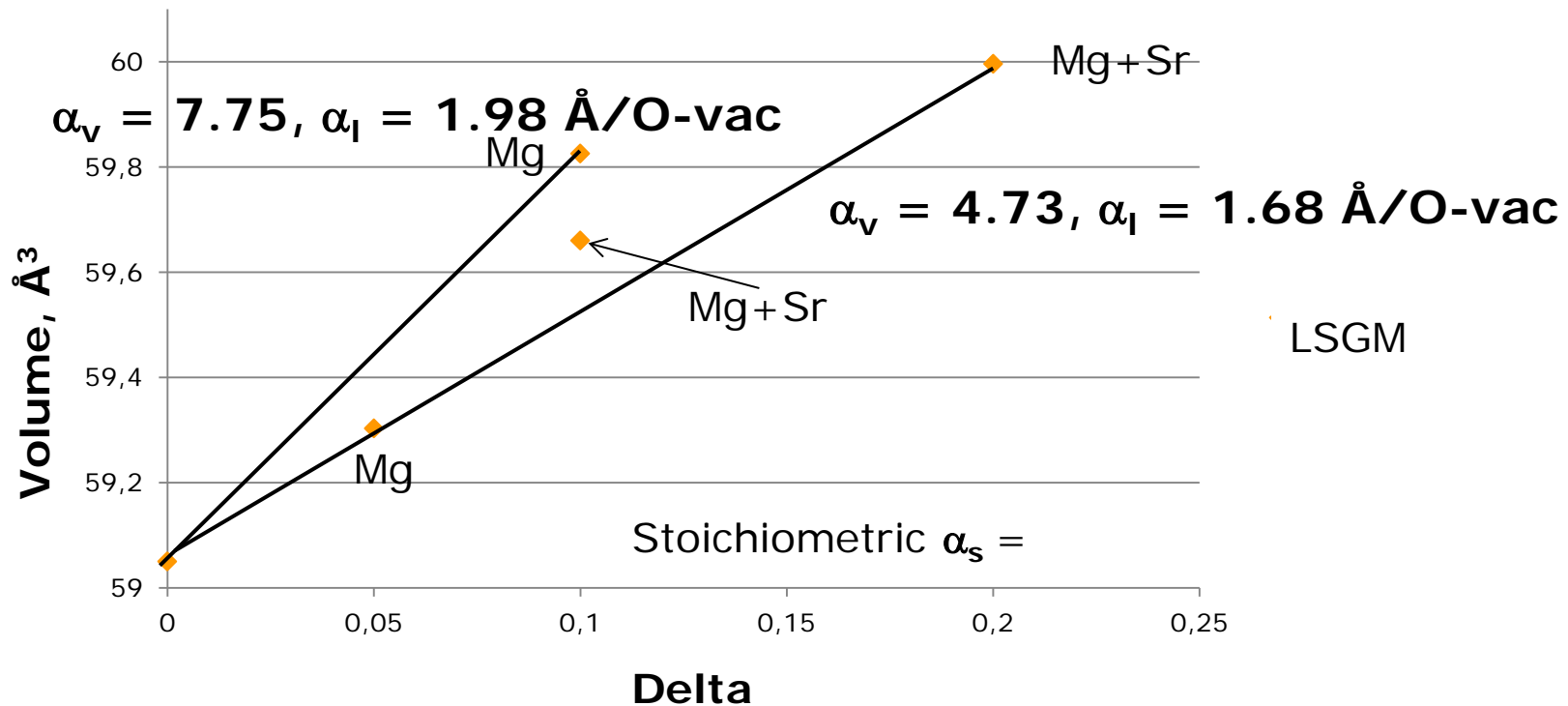
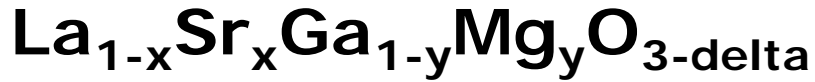


Most perovskites are not exactly cubic – and thus it is even more controversial to calculate vacancy volume in perovskites

From Cava Lab (J.R. Cava)

# "Ideal" perovskite data

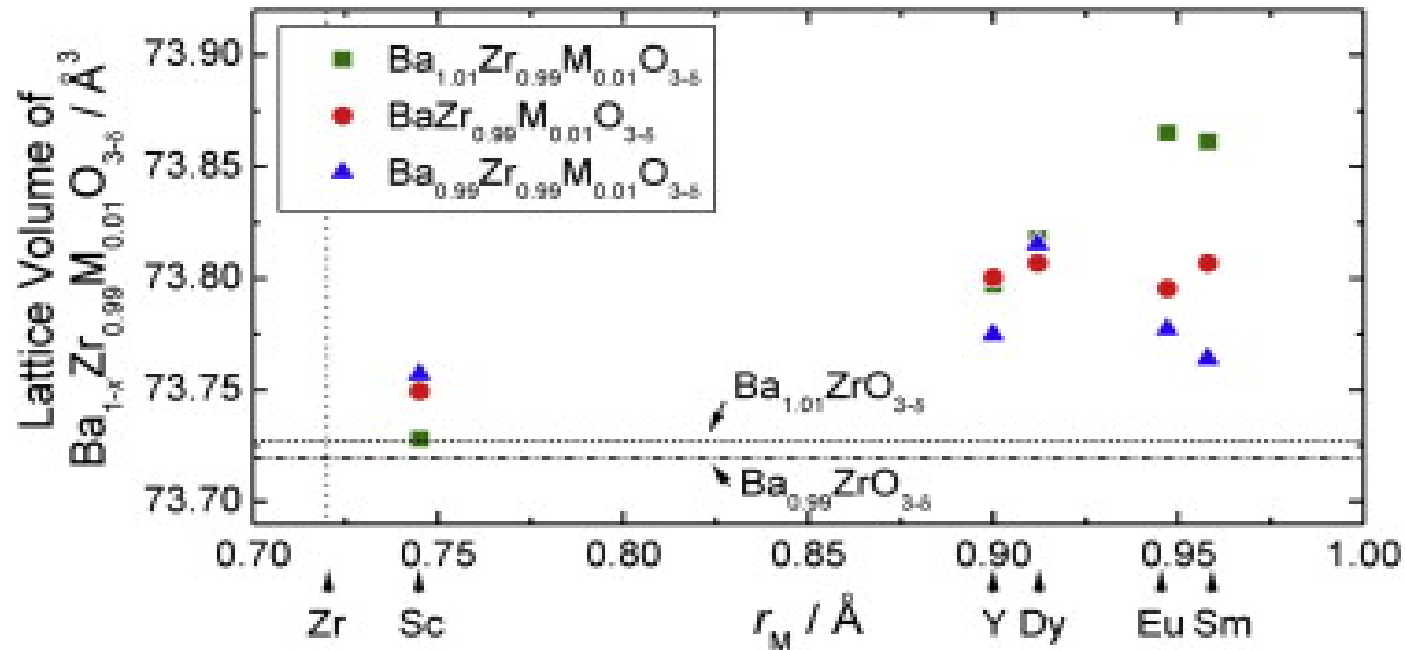
- $r_{\text{O}^{2-}} = 1.40 \text{ \AA}$
- $r_{\text{A,ideal}} = 1.40 \text{ \AA}$
- $r_{\text{B,ideal}} = 0.58 \text{ \AA}$
  
- $a = 3.96 \text{ \AA}$
  
- $V = 62.1 \text{ \AA}^3$



### Volume per formula unit versus oxygen sub-stoichiometry

Data from: M. Kajitani et al. *Chem. Mater.* 2003, **15**, 3468 and 2005, **17**, 4235 (neutron diffraction)

# BaZrO<sub>3</sub>



From: Donglin Han, Yoshitaro Nose, Kozo Shinoda, Tetsuya Uda  
 Solid State Ionics, **213** (2012) 2–7

$$r_{\text{Ba}} = 1.61 \text{ \AA}$$

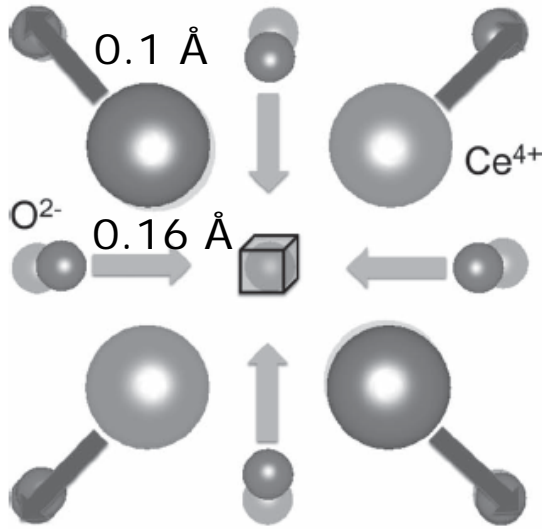
Introduction of OH<sup>-</sup> ( $r = 1.37 \text{ \AA}$ ) increases the unit cell volume with  $\approx 1/2 - 1 \%$ , i.e.  $r_v < 1.37 \text{ \AA} < r_{\text{O}^{2-}} = 1.40 \text{ \AA}$

# Conclusion

- **Introduction of oxide vacancy without introducing cations bigger than the corresponding host shrinks the unit cell volume in fluorite and perovskite structured metal oxides**
- **In fluorites  $r_v$  increase with decreasing metal – oxygen bond strength**
- **In perovskites the situation is more complicated, but due to the strong B-ion-oxygen bond the volume changes tend to be less than half of what is typically seen in fluorites**



# Lattice shrinking contribution of vacancies



Tuller et al 2012

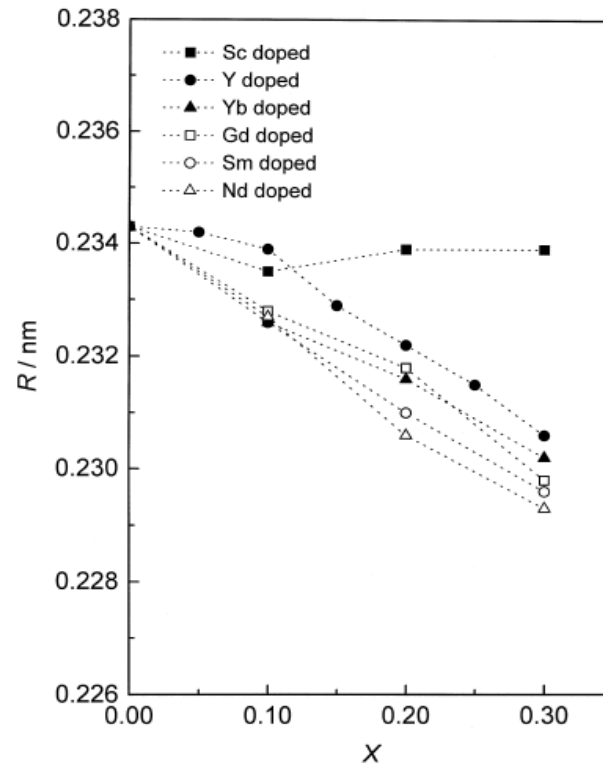
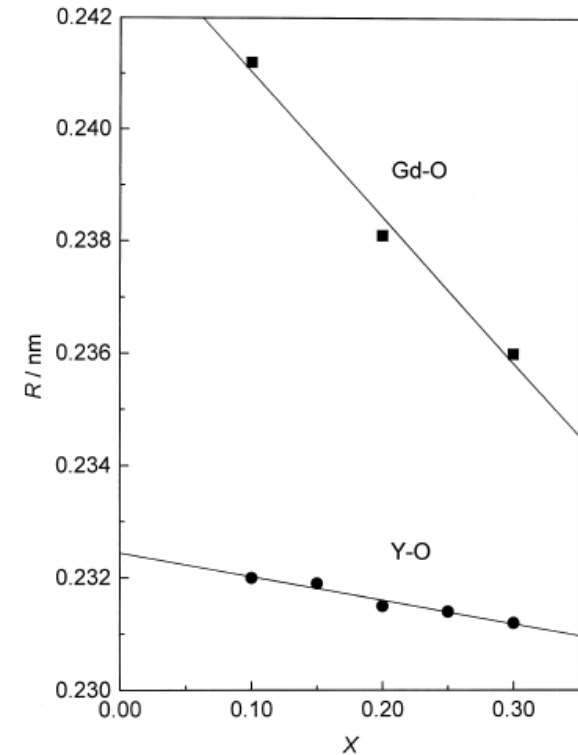


Fig. 4. The Ce-O inter-atomic distances in  $Ce_{1-x}Ln_xO_{2-x/2}$  as a function of Ln content (Ln=Sc, Yb, Y, Gd, Sm and Nd).



Yamazaki et al 2000

- EXAFS results (and computational simulations) support this relaxation pattern
- This means though that the local volume at a vacant oxide ion site is actually increasing!

# Model assumptions and limitations



- The cations have a coordination number less than 8 when the fluorite structure is acceptor doped and has vacancies, which affects their effective ionic radii. This difficulty is somewhat overcome by treating the vacancy as a species in the lattice possessing a certain radius.
- The oxygen vacancy radius is taken to be independent of concentration and dopant type.
- These calculations assume random distribution of the oxygen vacancies (and the dopant) and adopt a linear relationship between lattice parameter and dopant concentration (Vegard's law). Neither of these assumptions is true at higher dopant concentrations.
- The value of  $r_v$  does not represent the local structural modifications in the neighborhood of an oxide ion vacancy, but stems from the average lattice constant and acts as a parameter that includes all the structural complexity that is not accounted for by the model.

# More precise model by Nakamura 2010

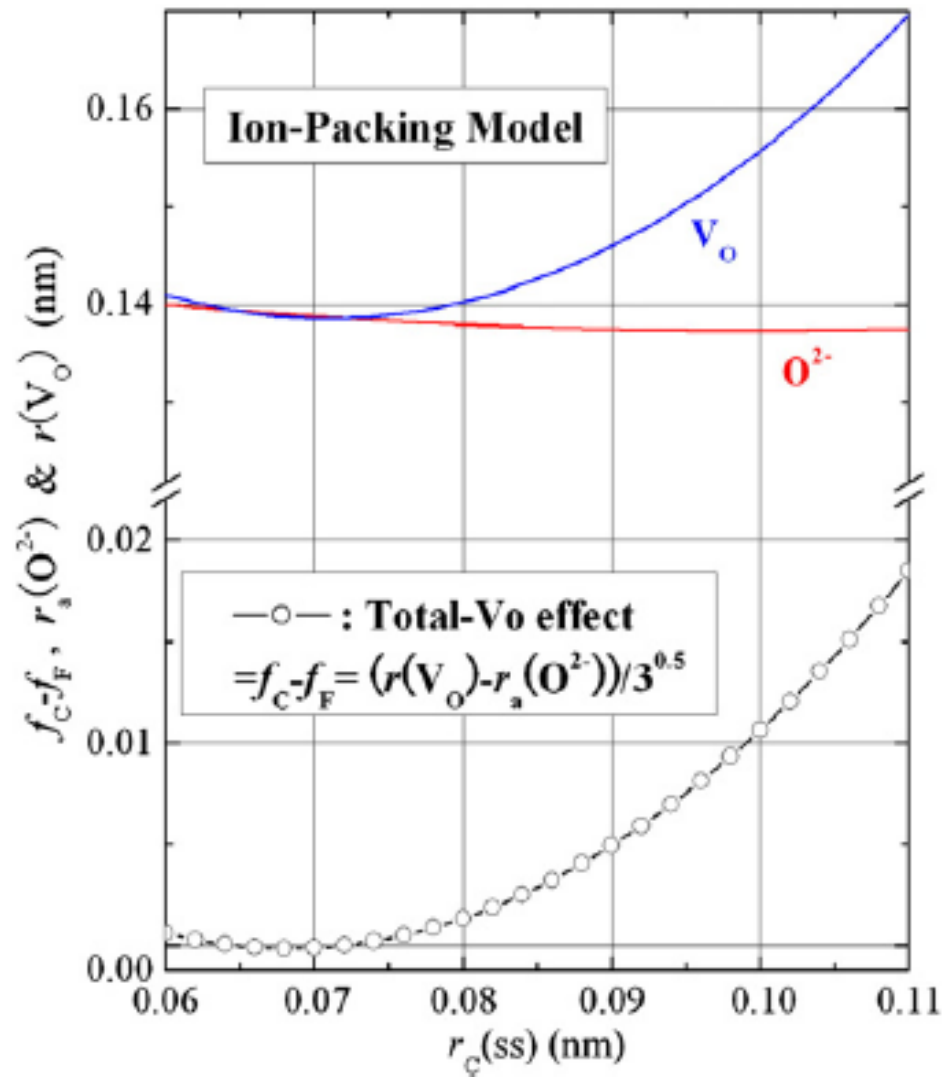


Fig. 10.  $r_a(O^{2-})$  (Eq. (23)),  $r(V_o)$  (Eq. (24)) and  $(f_c - f_F)$  (the total  $V_o$  effect in Eq. (22)) curves as a functional of  $r_c(ss)$  in the present Ion-Packing (I-P) model.