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Peroxide as a mechanism to accommodate excess oxygen

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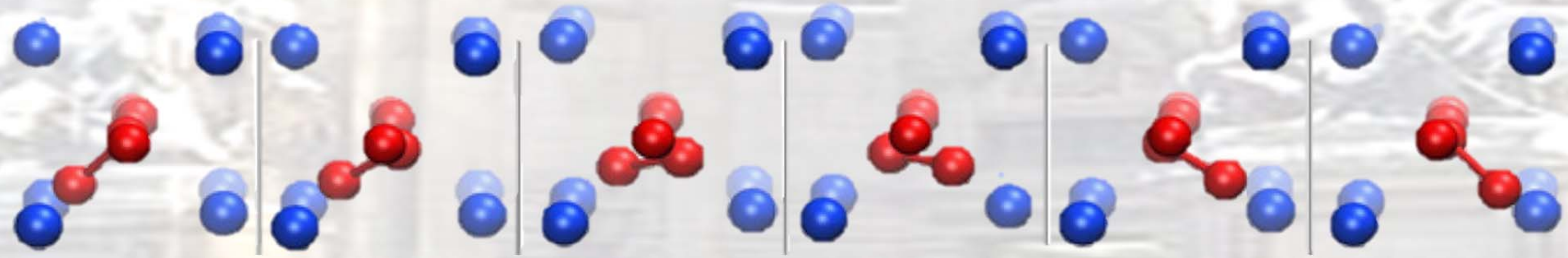
Peroxide as a Mechanism to Accommodate Excess Oxygen
Peroxide, the neglected defect process

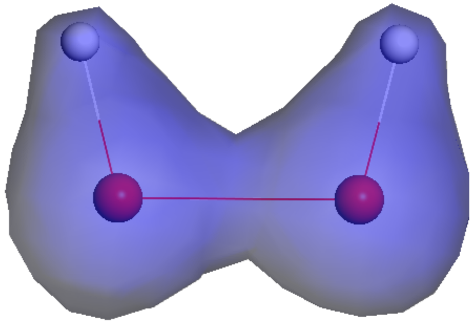


Simon Middleburgh & Robin Grimes

Outline

- The peroxide defect – has it been a bit neglected?
- Rock salt (MgO, CaO & BaO).
- Decomposition of BaO_2.
- Fluorite (UO_2, CeO_2 & ThO_2).
- Perovskite ($CaZrO_3$, $SrZrO_3$ & $BaZrO_3$)
- Theory vs. Experiment (Raman studies).
- Summary.

The Peroxide Ion

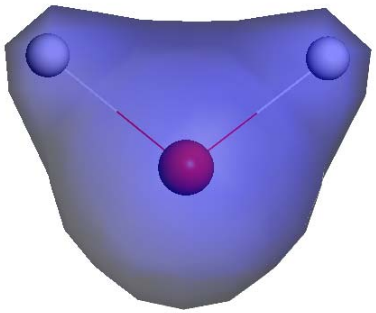


Hydrogen peroxide– H_2O_2

O_2^{2-} ion → O---O bond distance of ~1.47 Å

O---O bond stretch 878 cm^{-1}

Same charge – no need for charge compensating defects.



Water – H_2O

O^{2-} ion

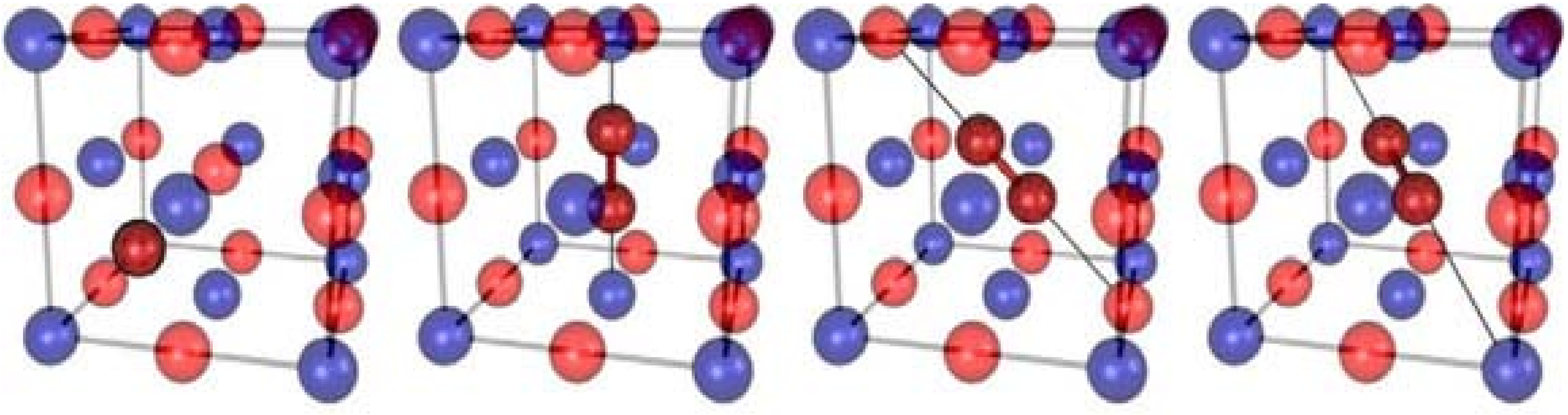
There is also the superoxide ion to be considered O_2^- (e.g. KO_2)

Crystallography

- All four alkali earths form MO and MO_2 structures.

Cation	Lattice parameter oxide (Å)	Lattice parameter dioxide (Å)
Mg	4.21 (4.24)	4.82 (4.8441)
		a, c (a, c)
Ca	4.79 (4.81)	3.29, 6.52 (3.56, 6.59)
Sr	5.15 (5.16)	3.51, 6.66 (3.55, 6.55)
Ba	5.55 (5.54)	3.79, 6.88 (3.75, 6.73)

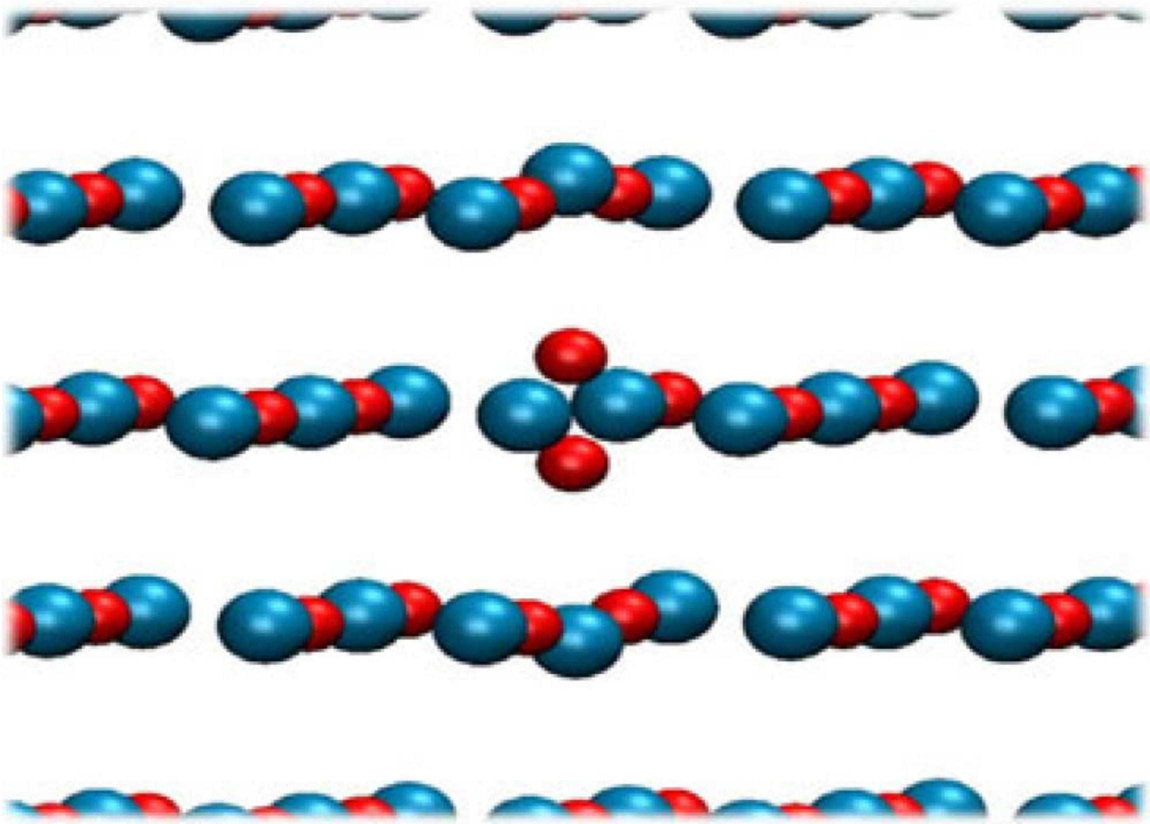
Accommodation of Excess Oxygen



O interstitial | <100> peroxide | <110> peroxide | <111> peroxide

In the rock salt structure the peroxide ion manifests as a ‘special’ split interstitial defect species.

Small distortion?



Rock Salt Structures: ½O_2 Solution Enthalpy

Lattice		Isolated int	Split int	<111> peroxide	<110> peroxide	<100> peroxide
MgO	Solution enthalpy (eV)	4.41	*	[illegible]	2.16	3.20
	O–O distance (Å)	–	*	[illegible]	1.45	1.38
	Defect volume (Å^3)+	13.92	*	[illegible]	11.18	14.34
CaO	Solution enthalpy (eV)	2.28	4.22	[illegible]	[illegible]	0.84
	O–O distance (Å)	–	2.52	[illegible]	[illegible]	1.40
	Defect volume (Å^3)+	11.40	19.74	[illegible]	[illegible]	9.04
SrO	Solution enthalpy (eV)	1.55	2.87	0.17	**0.08**	[illegible]
	O–O distance (Å)	–	3.58	1.47	1.46	[illegible]
	Defect volume (Å^3)+	11.34	24.94	12.16	11.73	[illegible]
BaO	Solution enthalpy (eV)	0.83	1.57	−0.36	−0.47	[illegible]
	O–O distance (Å)	–	2.91	1.47	1.47	[illegible]
	Defect volume (Å^3)+	10.65	14.91	12.20	12.08	[illegible]

*Gemetry relaxed to form the <111> peroxide defect with no barrier.

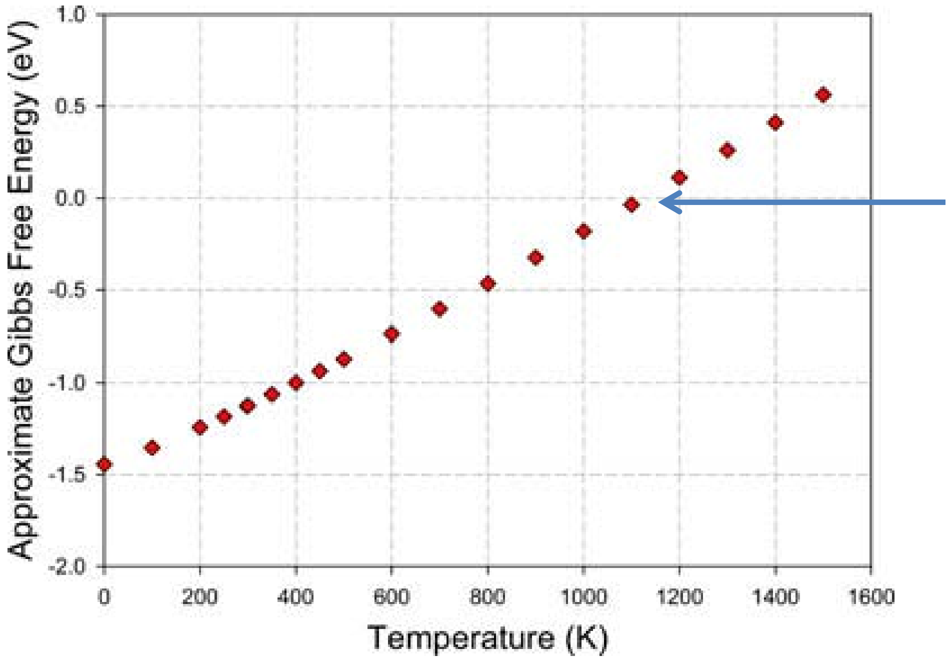
MgO
Forms a <111> peroxide
Positive energy, therefore difficult to form (although lower than all other defect energies!).

CaO
Forms a <110> peroxide or a <111> peroxide. Positive energy, therefore difficult to form – similar to MgO.

SrO and BaO
Forms a <100> peroxide with a negative energy. Interesting!

$\frac{1}{2}O_2 + BaO \rightarrow BaO_2$

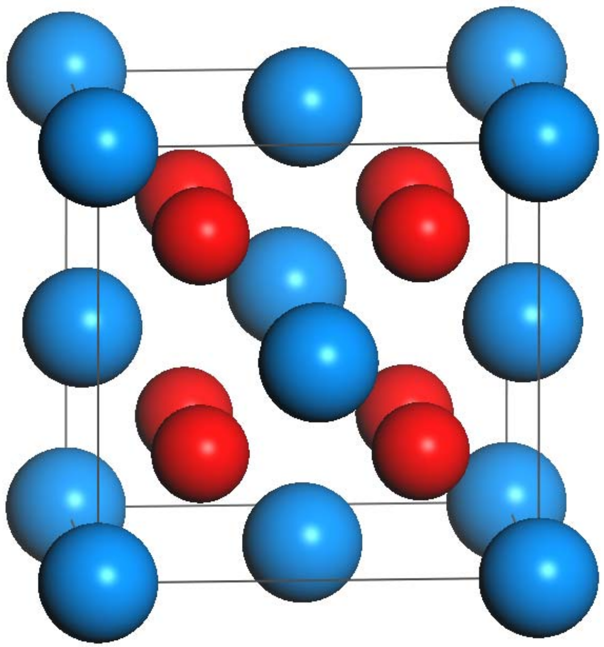
- Enthalpy of reaction is -1.15 eV
- By including the entropy associated with the O_2 molecule (JANAF table) one can estimate the temperature dependence

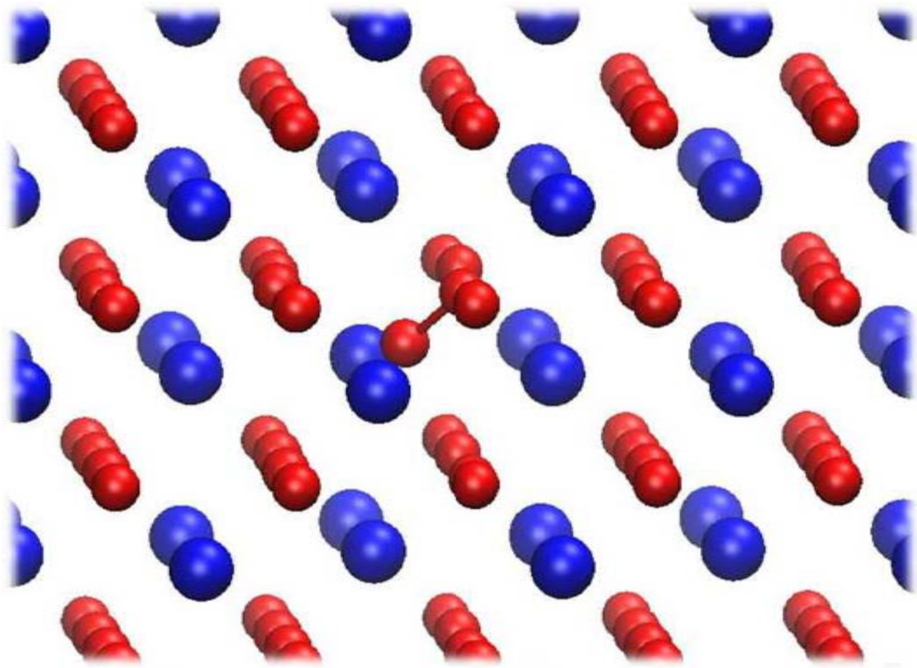


Decomposition at ~1100K. Experimental observation reports decomposition at 1175K… Pretty good!

- Prediction for SrO_2 decomposition is 800K
- CaO_2 and MgO_2 is 450 K (note different crystallography)

Fluorite Structure of CeO_2, ThO_2 and UO_2 Accommodating Excess Oxygen





In the fluorite structure the peroxide ion can shift from the oxygen site towards the (½, ½, ½) interstitial site.

Enthalpy for ½O_2 Solution into CeO_2, ThO_2 and UO_2

Oxygen defect	CeO_2	ThO_2	UO_2
Interstitial	3.24	1.84	
<100> split interstitial	[a]	[a]	[a]
<110> split interstitial	4.22 (2.13)	[a]	0.05 (2.41)
<100> peroxide	2.50 (1.40)	2.15 (1.44)	1.45 (1.44)
<110> peroxide	2.38 (1.42)	2.01 (1.45)	[b]
<111> peroxide			0.95 (1.49)

CeO_2
Peroxide the most preferable form (orientated in the <111> direction displaced towards the (½,½,½) interstitial site .

ThO_2
Similar to CeO_2. Large potitive energy indicating a low concentration of peroxide defects (lower than any other intrinsic defect in ThO_2.

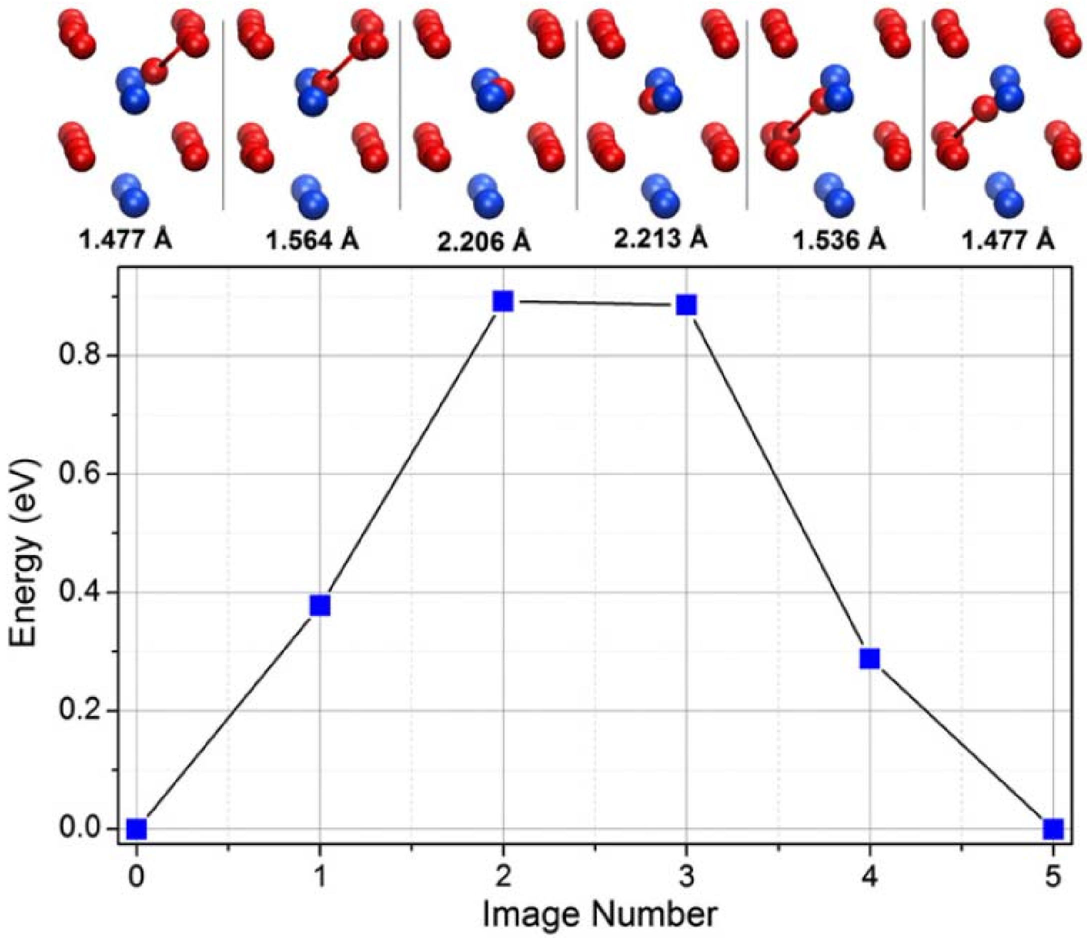
Difficult to oxidise cation from 4+ to 5+ charge

UO_2
Forms an interstitial defect as expected.

$U^{4+} \rightarrow U^{5+}$ easy in UO_2

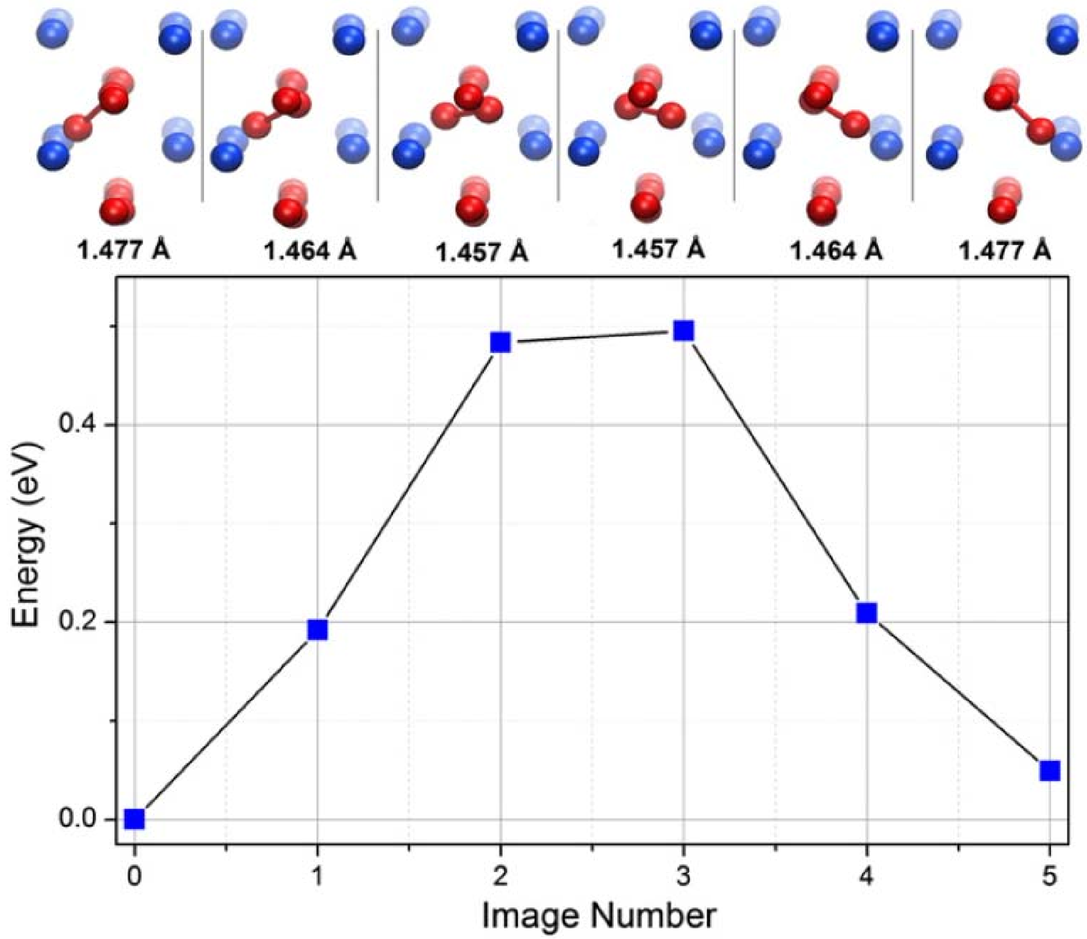
Transport: bond breaking

- Transport across the lattice requires two steps
- 1st involves a single O interstitial intermediate
- Activation energies:
  ThO_2, 0.89 eV
  CeO_2, 1.25 eV



Transport: rearrangement

- 2nd involves rearrangement of a peroxide molecule
- Activation energies: ThO_2, 0.50 eV CeO_2, 0.38 eV
- So transport is limited by the 1st



Reaction of Oxygen into Zirconates

DFT Calculations using standard GGA potentials using the VASP code.

$$\frac{1}{2}O_2 \rightarrow O_i$$

$$\frac{1}{2}O_2 + O_O \rightarrow \{V_O : 2O_i\}_{\text{split interstitial}}$$

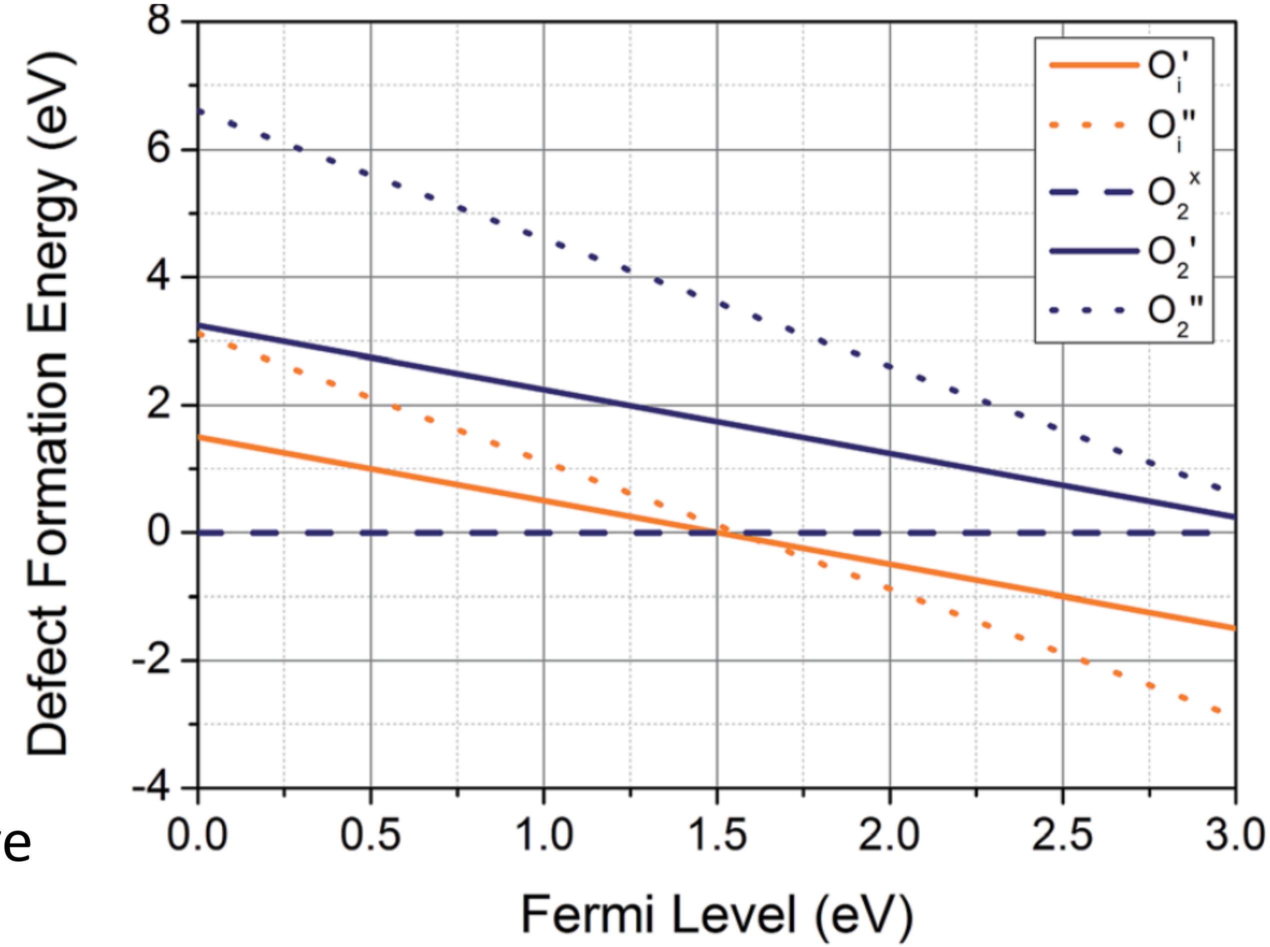
$$\frac{1}{2}O_2 + O_O \rightarrow \{V_O : 2O_i\}_{\text{peroxide ion}}$$

Reaction	$BaZrO_3$	$SrZrO_3$	$CaZrO_3$
$\frac{1}{2}O_2 \rightarrow O_i$	2.43 eV	1.40 eV	0.89 eV
split interstitial	------------	------------	------------
peroxide ion	-0.01 eV	0.1 eV	0.22 eV

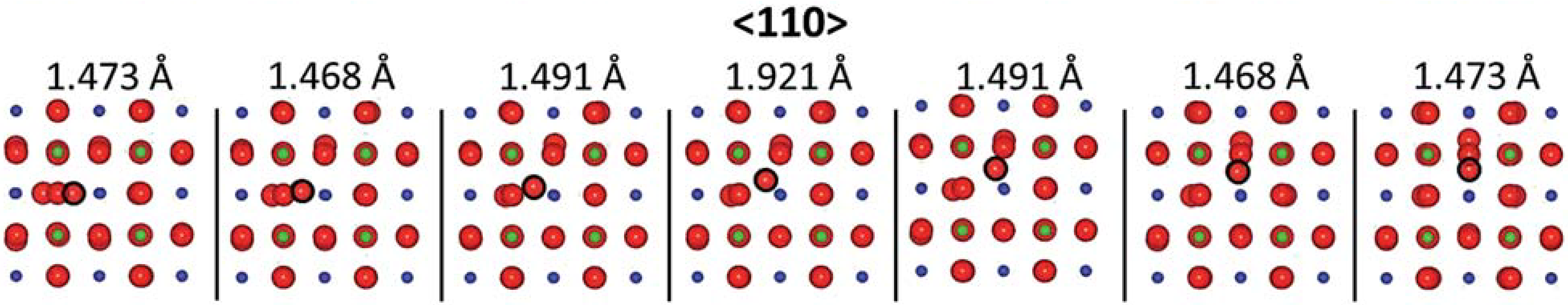
Reaction of Oxygen into $BaZrO_3$

$$E_f = E_{D,q} - E_P + \frac{1}{2}\mu_{O_2} + q\mu_e + E_{MP}$$

- E_f formation energy
- μ_e Fermi level
- E_{MP} Makov–Payne
- μ_{O2} chemical potential
- E_P total energy perfect
- $E_{D,q}$ total energy defective



Oxygen Migration



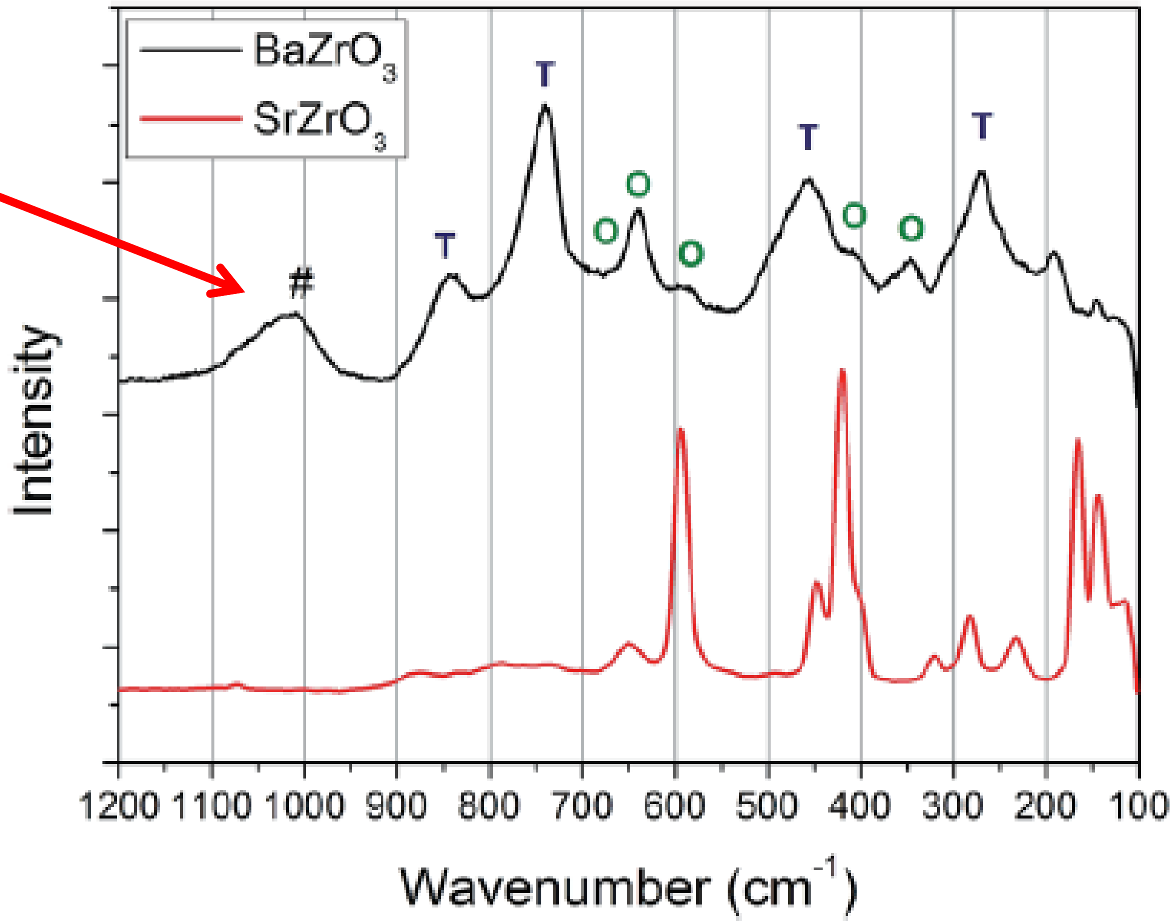
- Migration in <110> favoured over <100>
- Tetragonal $BaZrO_3$: 0.78 eV
- Orthorhombic $BaZrO_3$: 0.75 eV
- Orthorhombic $SrZrO_3$: 0.82 eV
- Orthorhombic $CaZrO_3$: 0.83 eV
- Values similar to V_o mediated processes in perovskites

Experimental 'support'

- This was experimentally examined by carrying out Raman spectroscopy measurements to look for a peak indicative of peroxide ions.
- First on as produced $BaZrO_3$ and $SrZrO_3$
- Then finely ground powders of $BaZrO_3$ and $SrZrO_3$ were treated in 30 wt% H_2O_2 solution for 150 hours.
- Predicted bond stretch of 996 cm^{-1} for $BaZrO_3$
  980 cm^{-1} for $SrZrO_3$

Raman of $BaZrO_3$ and $SrZrO_3$

O-O stretching mode

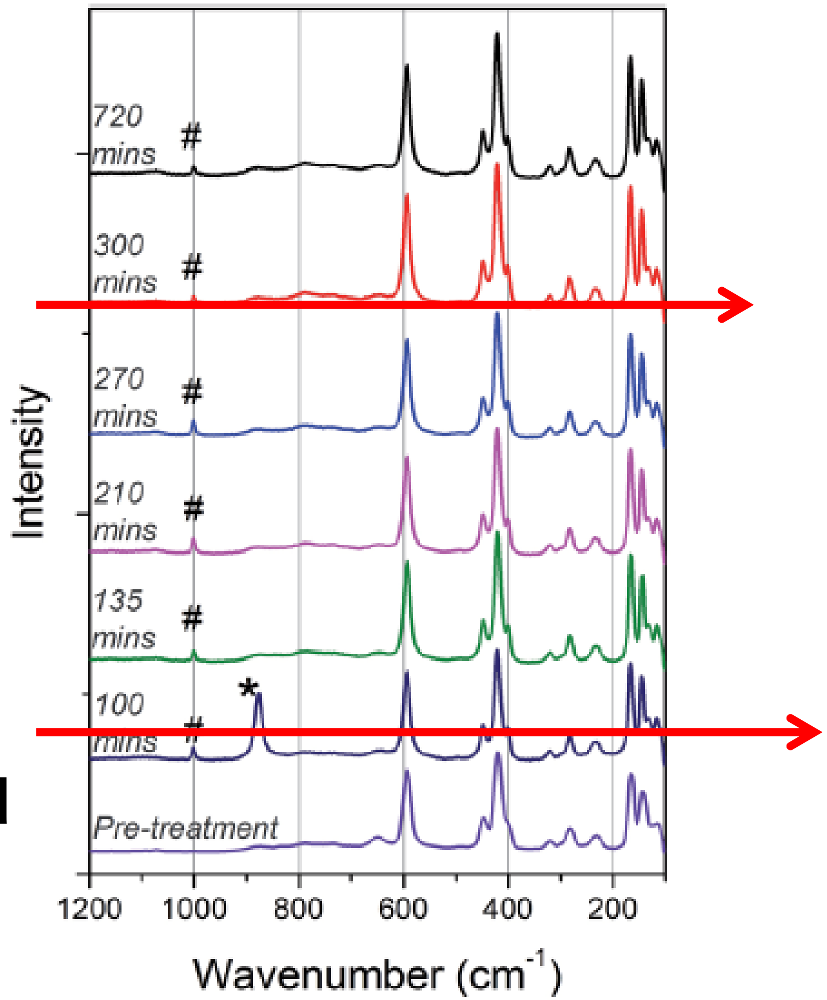


Raman of $SrZrO_3$ after H_2O_2 Treatment

New Peaks

1000 cm^{-1}
Simulation suggests O_2^{2-} ion

870 cm^{-1}
H_2O_2 adsorbed on surface



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Accommodation of Excess Oxygen in Group II Monoxides

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Accommodation of excess oxygen in fluorite dioxides

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Peroxide defect formation in zirconate perovskites

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Summary

- The dominant defect in group II monoxides is the peroxide ion. Decomposition of BaO_2 to go to BaO with temperature agrees well with experiment.
- Excess oxygen is accommodated by peroxide ions in CeO_2 and ThO_2 but not UO_2.
- Transport is limited by bond breaking with O_i intermediary.
- Excess oxygen predicted to be accommodated in $BaZrO_3$ and $SrZrO_3$ by peroxide ions, for lower Fermi level values.
- Activation energies again ~0.8 eV, similar to V_o mediated.
- Raman on treated and un-treated zirconate powders predict formation of $BaZrO_{3+x}$ and $SrZrO_{3+x}$.
- Further work: peroxide in Al_2O_3.