Electrical heterogeneity and anomalous conductivity behaviour in reduced titanates.

$Ba_{1-x}La_xTi_{1-x/4}O_{3-\delta}$

$Sr_{1-3y/2}La_yTiO_{3-\delta}$

$EuTiO_{3-\delta}$
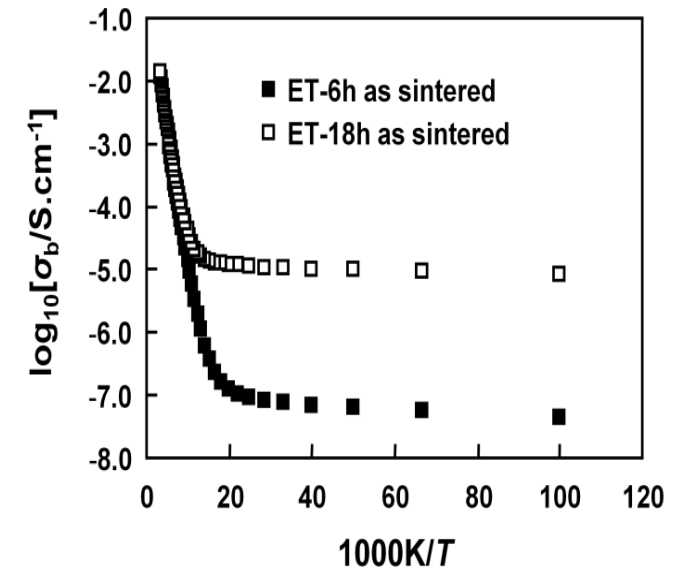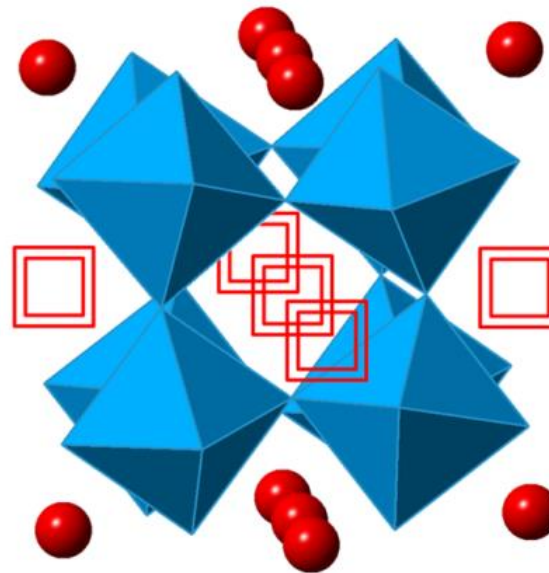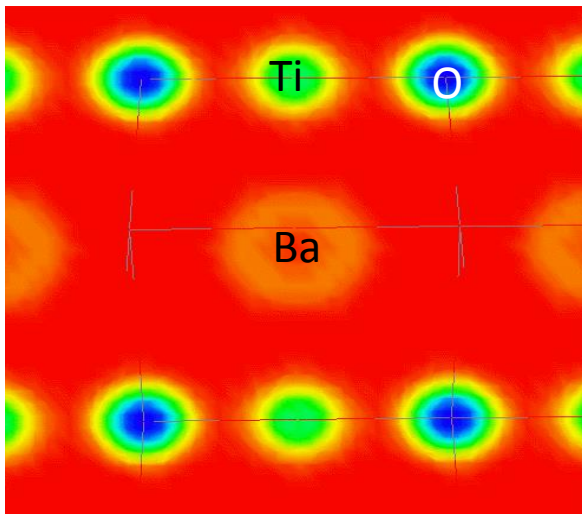
Derek C Sinclair

Department of Materials Science & Engineering

Sheffield, UK

d.c.sinclair@sheffield.ac.uk

Acknowledgements

Topics

- **Background:** Doping Mechanisms

- **Topic 1:** La-doped $ATiO_3$ (A= Ba, Sr) Influence of doping mechanisms and metal vacancies on reduction characteristics.

- **Topic 2:** $EuTiO_3$ (and related titanate-based perovskites) often show anomalous temperature-independent conductivity < 100 K . Origin?
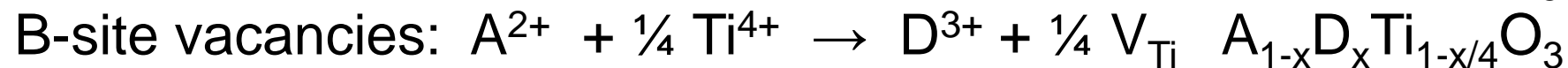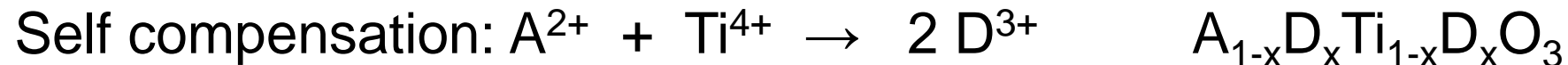
- **Conclusions.**

Background

- Doping Mechanisms in $A^{2+}Ti^{4+}O_3$ perovskites.

- Oxygen-loss: $O^{2-} \rightarrow \frac{1}{2}O_2\ (g) + 2\ e^- + V_O$

$$2\ Ti^{4+} + 2\ e^- \rightarrow 2\ Ti^{3+} \quad (ATi^{4+}_{1-x}Ti^{3+}_xO_{3-x/2})$$
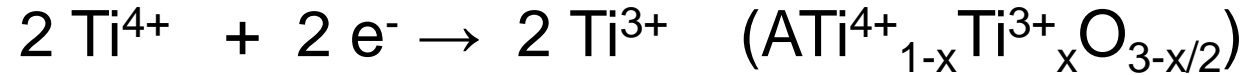
- Donor doping: (eg La^{3+} for Ba or Sr)

$D^{3+} + e^- \rightarrow A^{2+}$ (electronic doping) $A_{1-x}D_xTi^{4+}_{1-x}Ti^{3+}_xO_3$

However, ionic compensation is also possible!

A-site vacancies: $3\ A^{2+} \rightarrow 2\ D^{3+} + V_A \qquad A_{1-3x}D_{2x}TiO_3$

Self compensation: $A^{2+} + Ti^{4+} \rightarrow 2\ D^{3+} \qquad A_{1-x}D_xTi_{1-x}D_xO_3$

B-site vacancies: $A^{2+} + \frac{1}{4}Ti^{4+} \rightarrow D^{3+} + \frac{1}{4}V_{Ti} \quad A_{1-x}D_xTi_{1-x/4}O_3$
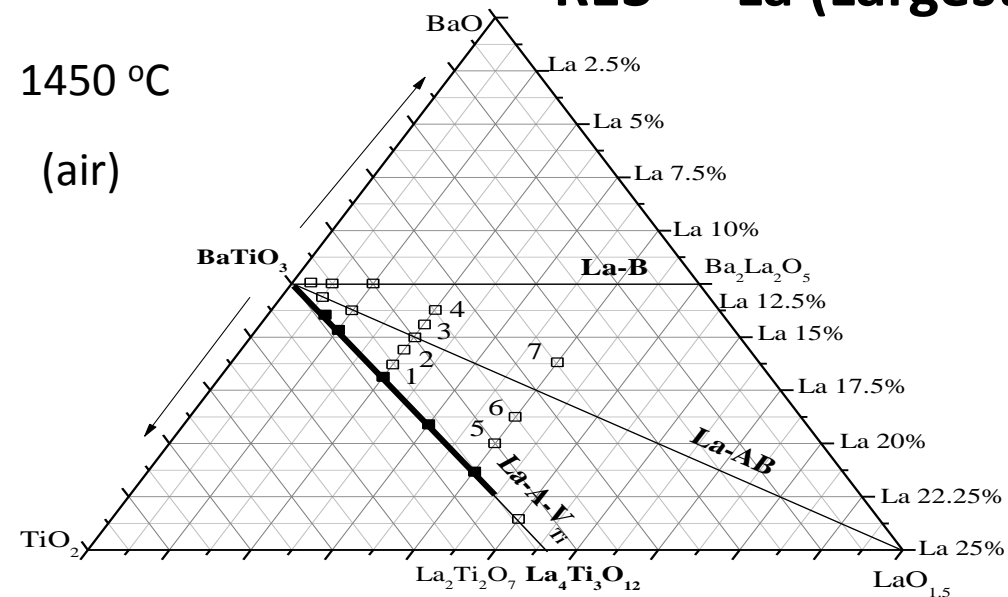
Big Question: which mechanism dominates and do we have an issue with thermodynamics versus kinetics, especially in bulk ceramics.
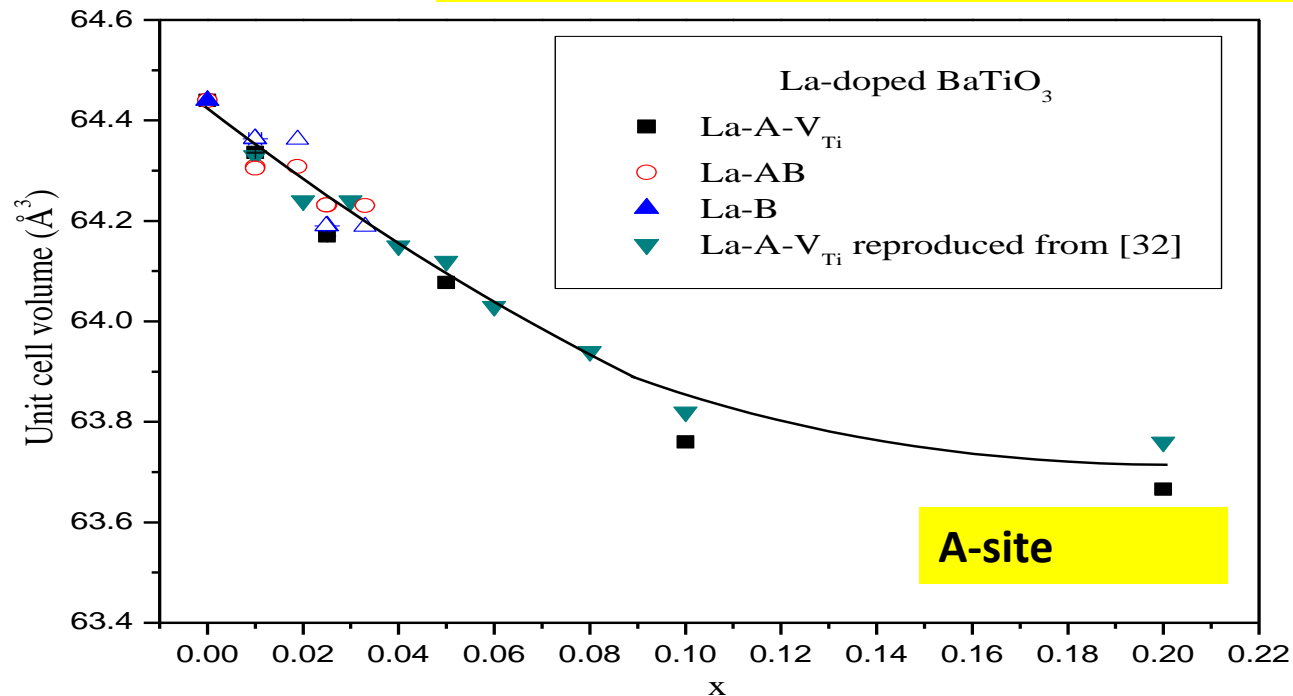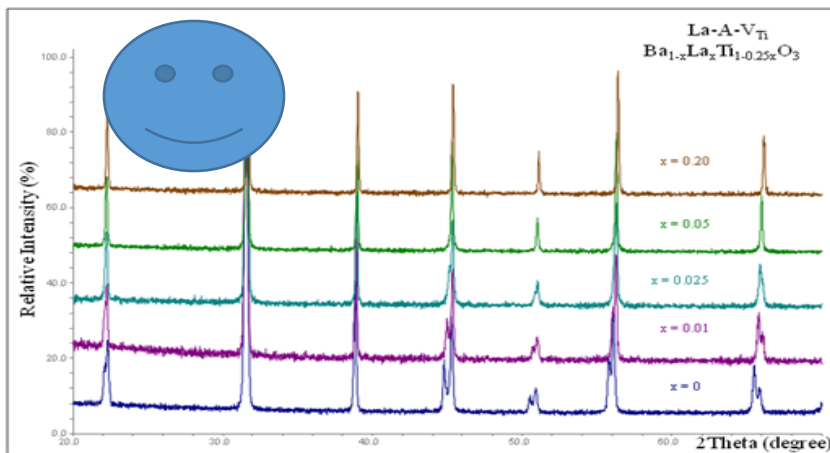
RE3+ = La (Largest RE)

1450 °C

(air)

A-site
(Ti-vacancies)

$Ba_{1-x}La_xTi_{1-x/4}O_3$ $0 \leq x \leq 0.20$

A-site

$Ba_{1-x}La_xTi_{1-x/4}O_3$ $0 \leq x \leq 0.20$
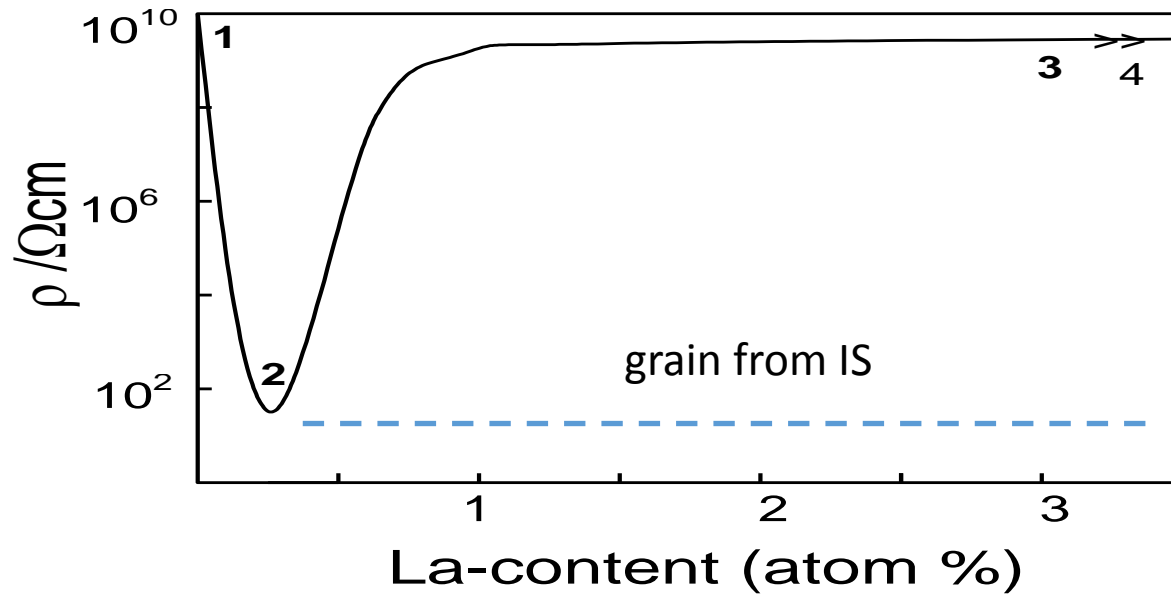
- r_{12} Ba = 1.61 Å   and La = 1.36 Å

- r_6 Ti = 0.605 Å   and La = 1.032 Å

- $\Delta A = r_{Ba} - r_{La} = 0.25$ Å

- La substitutes exclusively on the A-site.

- No evidence for extensive ss via electronic compensation (donor-doping) mechanism for samples prepared in air or O_2 at 1350 °C.

The doping mechanism in La-BaTiO$_3$

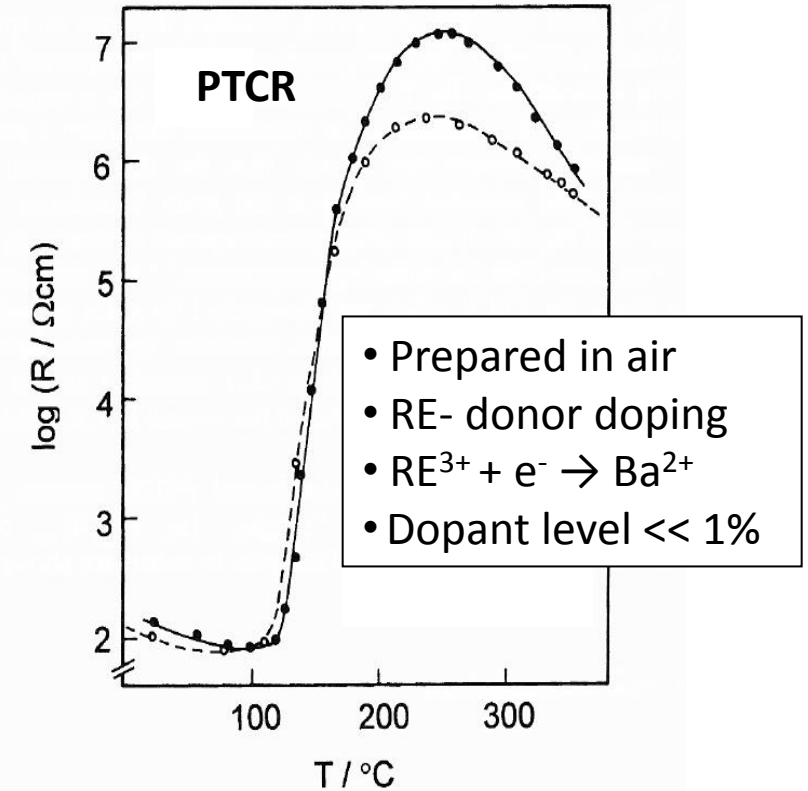**Is there a change in doping mechanism with La-content?**

Low x : donor (electronic) doping, La^{3+} + e$^-$ → Ba^{2+}

High x : Ionic compensation, La^{3+} → Ba^{2+} + ¼ Ti^{4+}

R$_{min}$ is obtained for 0.3 -0.5 atom % doping (ptcr devices) heated in at air > 1350 °C followed by rapid cooling.

- Prepared in air
- RE- donor doping
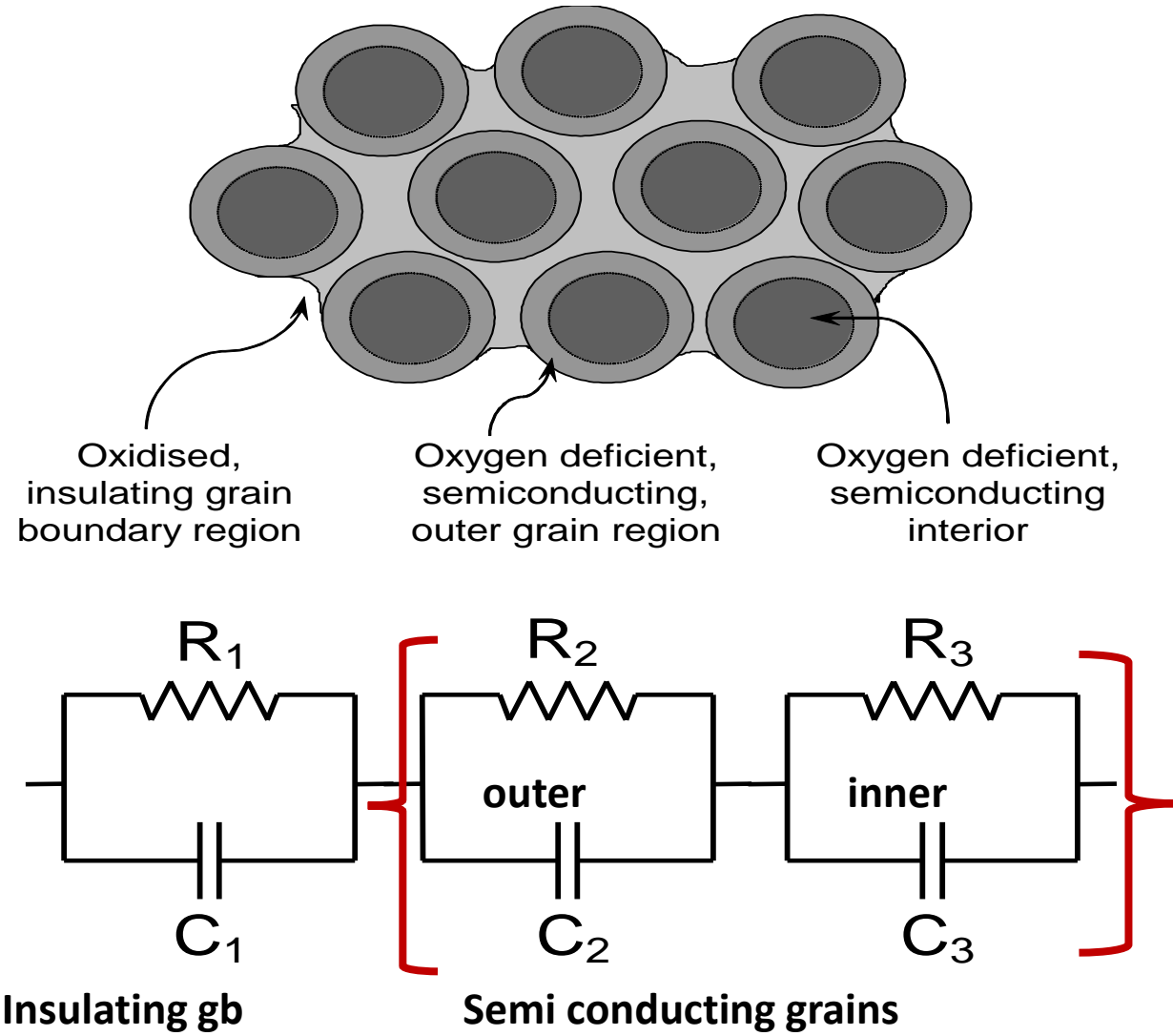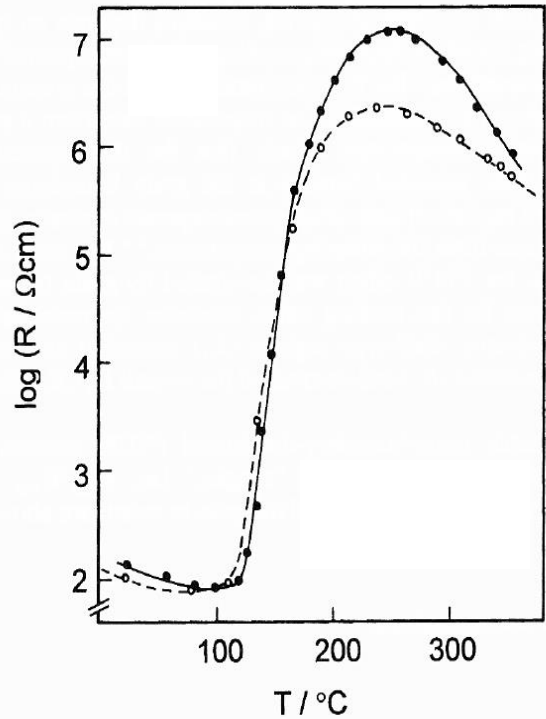- RE^{3+} + e$^-$ → Ba^{2+}
- Dopant level << 1%

- RE used to induce semiconductivity

Atomistic simulations from Lewis and Catlow (1986) suggested donor doping to be energetically more favourable

[1] G. V. Lewis and C. R. A. Catlow, J. Phys. Chem. Solids, **47** (1986) 89-97

Electrical microstructure for x = 0.003 (La) prepared in <u>air</u> at 1350 ºC

- Ea (bulk) ~ 0.06 - 0.1 eV

    (n-type)

- Ea (gb) ~ 0.9 – 1.2 eV

Oxidised, insulating grain boundary region

Oxygen deficient, semiconducting, outer grain region

Oxygen deficient, semiconducting interior

R_1 R_2 R_3

outer   inner

C_1 C_2 C_3

Insulating gb   **Semi conducting grains**

log (R / Ωcm)

T / ºC

F.D. Morrison, D.C. Sinclair and A.R West, J. Am. Ceram. Soc., <u>84</u> [3] (2001) 531-38.
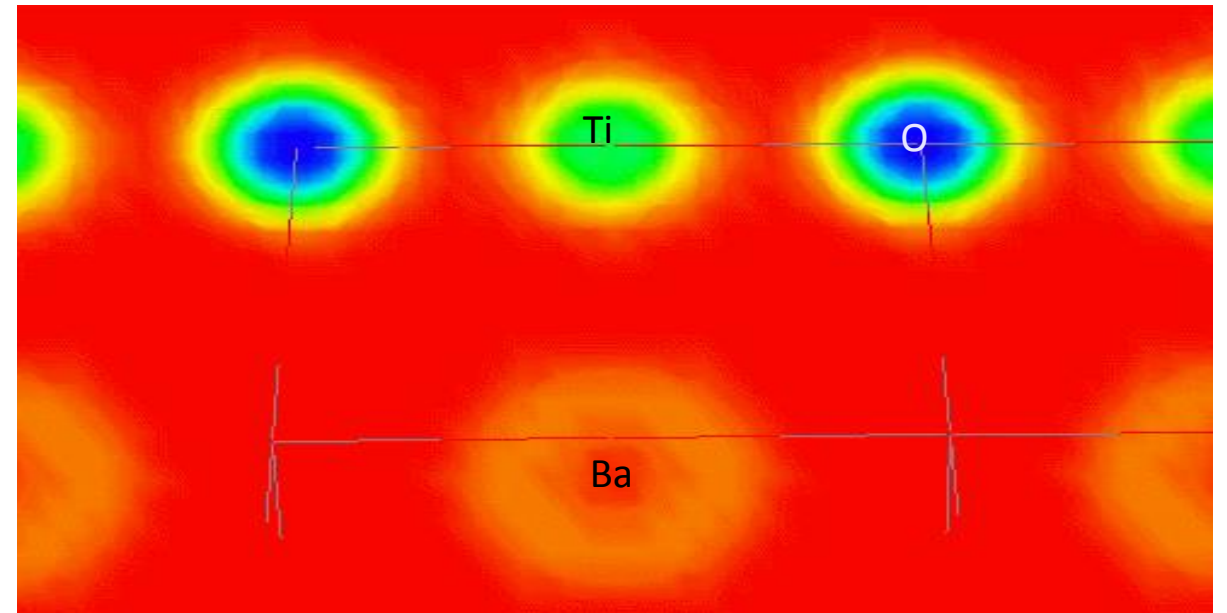
BaTiO$_3$ Model Development

Objectives

Previous simulations fail to describe defect chemistry because end members (BaO, TiO$_2$) are not energetically correct. Therefore the energetic balance for solution chemistry of defects is wrong. Design potential that models the entire range.

New Model Features

Ab initio methods have shown that the Ti-O bond has a degree of covalency. It is now represented with a partially bonding term (Lennard-Jones) rather than a full ionic description.

Angular (three-body) terms added for the O-Ti-O interaction to account for strain effects in the TiO$_6$ octahedra.

[1] G. V. Lewis and C. R. A. Catlow, J. Phys. Chem. Solids, **47** (1986) 89-97

Structure	Cohesive Energy (eV)	
	Experiment	Lewis and Catlow [1]
TiO$_2$ (rutile)	-125.5	-112.47
BaO	-31.90	-34.57
c-BaTiO$_3$	-159.86	-148.02
h-BaTiO$_3$	-159.73	-147.69

BaTiO$_3$ Model Development - Results

Structure	Lattice/Cohesive Energy (eV)		
	Experiment	Lewis and Catlow [1]	This work [2]
TiO$_2$ (rutile)	-125.5	-112.47	-129.49
BaO	-31.90	-34.57	-31.72
c-BaTiO$_3$	-159.86	-148.02	-160.02
h-BaTiO$_3$	-159.73	-147.69	-160.85

Structure	Lattice parameters		
	Experiment	Lewis and Catlow [1]	This work [2]
c-BaTiO$_3$	4.012\90.0	3.960\90.0	4.105\90.0
h-BaTiO$_3$	5.724\13.965\90.0\120.0	5.669\14.008\90.0\120.0	5.962\14.550\90.0\120.0

[1] G. V. Lewis and C. R. A. Catlow, J. Phys. Chem. Solids, **47** (1986) 89-97
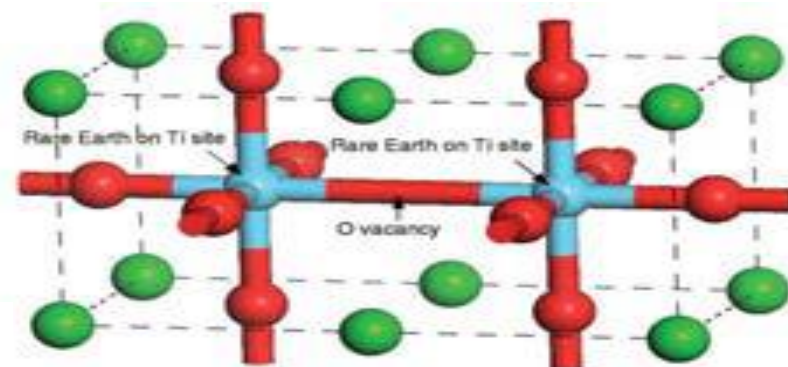
[2] C.L. Freeman, J.A. Dawson, H-R Chen, J.H. Harding, L. Ben and D.C. Sinclair, . J. Mater. Chem., **21** (2011) 4861–4868.

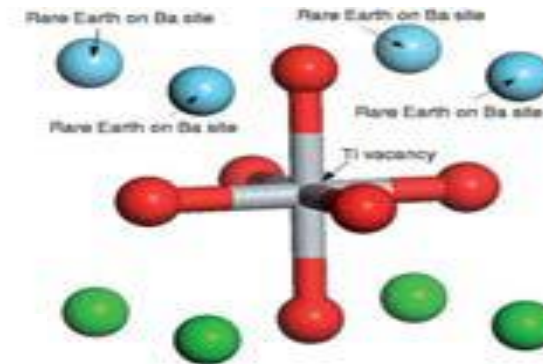# Sheffield Model : ionic compensation mechanisms

- **A-site with Ti-vacancies**
- **B-site with O-vacancies**
- **Self-compensation**

Yb   Gd   La

Legend: Ba, Ti, Self

Axis labels: Solution Energy (eV) vs Ionic Radii (A)
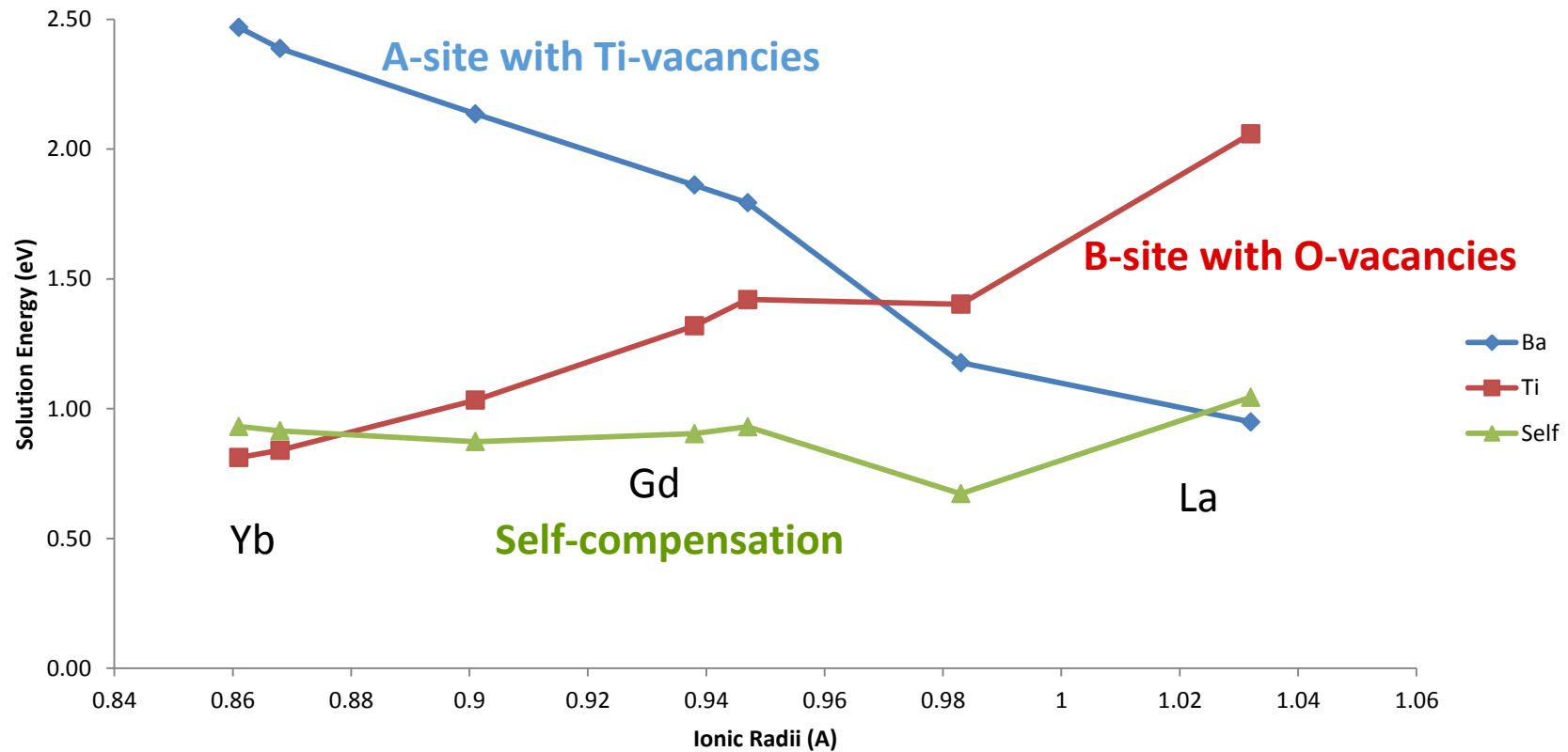
• **Excellent agreement between experimental results and simulations.**

Yb   La

Revised Model: Colin Freeman (Sheffield) Potentials

Electronic Compensation (Donor doping)
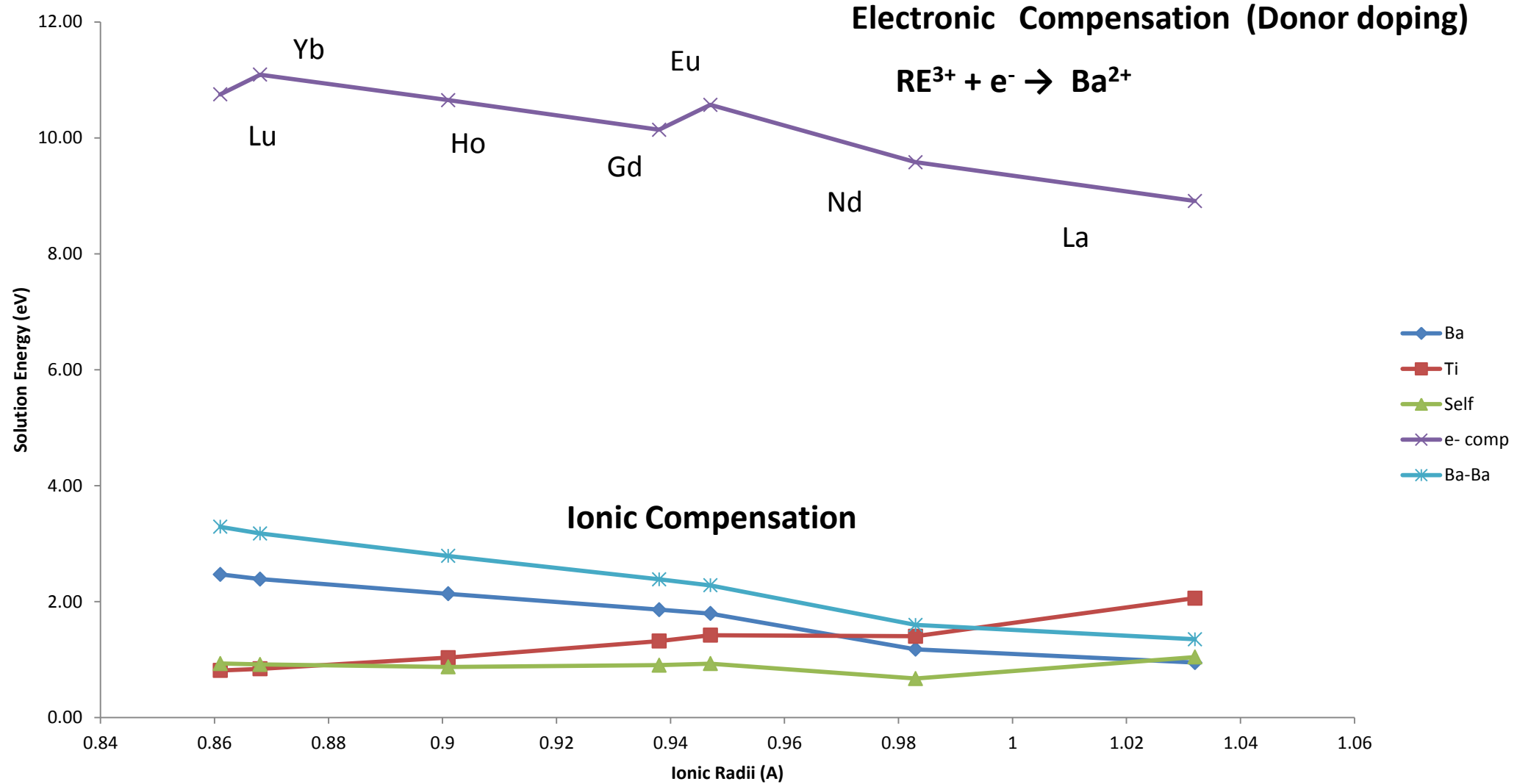
$$RE^{3+} + e^- \rightarrow Ba^{2+}$$

- Donor doping on A-site is very unfavourable : $RE^{3+} + e^- \rightarrow Ba^{2+}$

C.L. Freeman, J.A. Dawson, H-R Chen, J.H. Harding, L. Ben and D.C. Sinclair, . J. Mater. Chem., **21** (2011) 4861–4868.

Electron Compensation – Sheffield model vs. Lewis & Catlow model

Solution Energy (no binding) (eV)

Dopant	Lewis & Catlow model	Sheffield model
La^{3+}	0.22	9.06
Gd^{3+}	0.70	10.21
Er^{3+}	0.97	-
Yb^{3+}	-	11.2

Why??

$Ti_{Ti}^{\bullet}$ Ti^{3+} substitution at Ti^{4+} site requires more energy in Sheffield model (48.03 eV) compared to the L&C model (36 eV)

Alternative mechanism for semiconductivity is required!!

Suggestion: is oxygen loss the source of semiconductivity for samples processed in air?

Calculations for La from the Freeman (Sheffield) model.

Solution energy

- (1) Donor doping of RE $(RE^{3+} + e^- \rightarrow Ba^{2+})$ **9.06 eV**

- (2) Ti-vacancy formation $(RE^{3+} \rightarrow Ba^{2+} + \frac{1}{4} Ti^{4+})$ 1.01 eV

- (3) Oxygen-loss after Ti-vacancy formation $(O^{2-} \rightarrow \frac{1}{2} O_2 + 2e^-)$ 4.59 eV

(1) $Ba_{1-x}La_xTiO_3$ **9.06 eV**

(2) + (3) = $Ba_{1-x}La_xTi_{1-x/4}O_{3-\delta}$ **5.60 eV**

- No need to invoke a change in doping mechanism at low levels of doping for samples prepared in air.

- The process of oxygen-loss from samples containing Ti-vacancies is still energetically more favourable than direct donor-doping.

- This reconciles our electrical data and the phase diagram studies.

*C.L. Freeman, J.A. Dawson, J.H. Harding, F.D. Morrison, A.R. West and D.C. Sinclair, Adv. Functional Mater. **23** (2013) 3925-28*

Doping mechanisms in La-doped SrTiO$_3$

A-site vacancy

$3\ Sr^{2+} \longrightarrow 2\ La^{3+}$

$Sr_{1-3y/2}La_yTiO_3$

$y = 0.10$

Electronic (Donor doping)

$Sr^{2+} \longrightarrow La^{3+} + e^-$

$x = 0.10$

$Sr_{1-x}La_xTiO_3$

B-site vacancy

$Sr^{2+} + ¼\ Ti^{4+} \longrightarrow La^{3+}$

$z = 0.10$

$Sr_{1-z}La_zTi_{1-z/4}O_3$
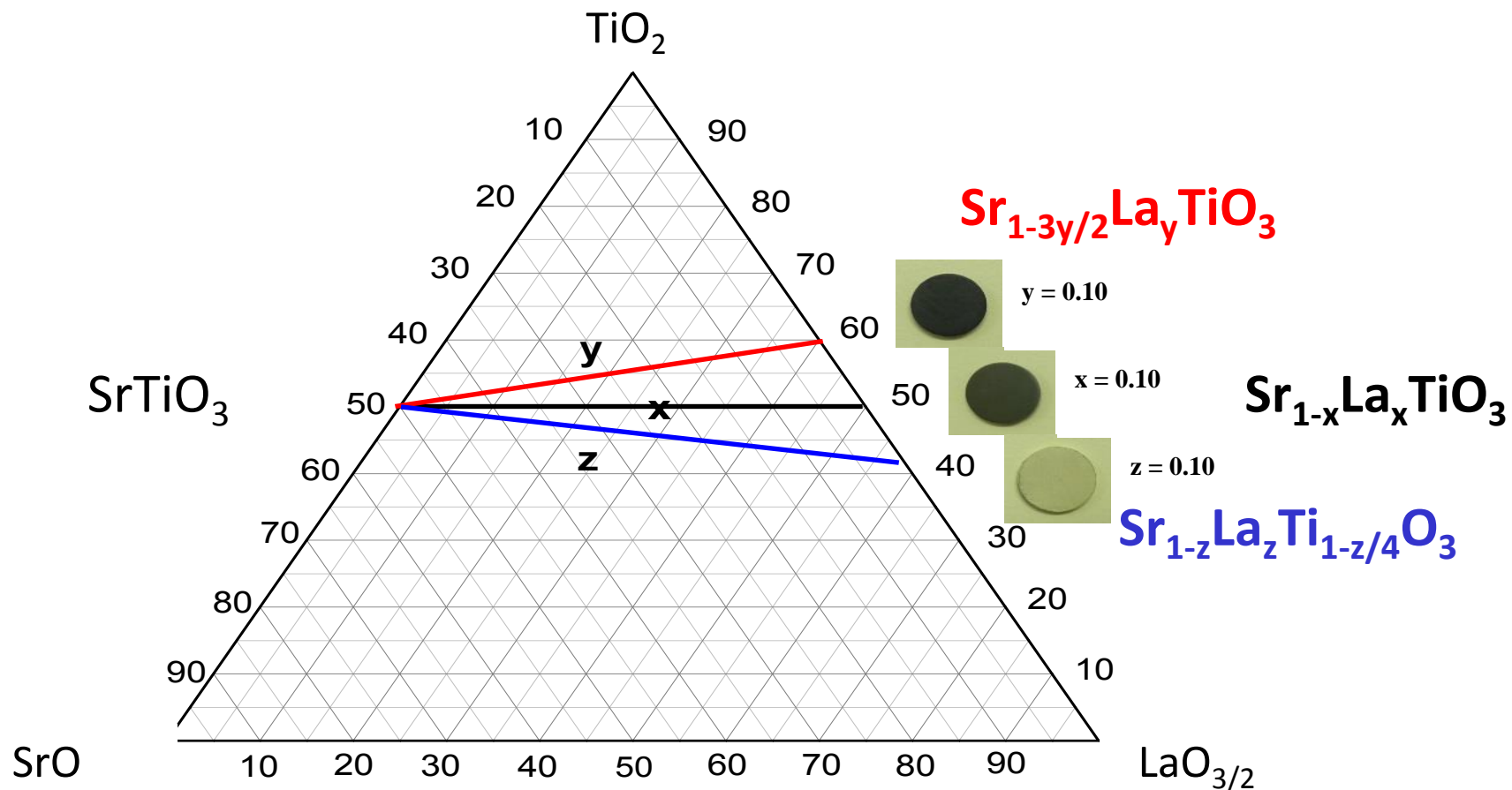
Solid solution limits in air (1500 °C)

$0 \leq x \leq 0.30$; $0 \leq y < 0.65$ (~ full solid solution); $0 \leq z \leq 0.15$

All single-phase ceramics (x, y, z = 0.10) sintered in flowing O$_2$ at 1500 °C
Bulk conductivity is highest for A-site vacancy (y = 0.10) sample!
Note: electrical properties are very dependent on processing conditions

Resistive surface layers and non-ohmic contact problems: Impedance Spectroscopy (IS)

Undoped SrTiO$_{3-\delta}$ ceramic processed in 5 % H$_2$/95% H$_2$ at 1500 ^oC for 6 hrs

- Oxygen-loss: $O^{2-} \rightarrow \frac{1}{2} O_2 (g) + 2 e^- + V_O$

(a)

(b)

Unpolished

Polished

Resistive surface layer that can be removed by polishing

Semiconducting/metallic oxide

Non-ohmic contact

Too conductive to measure by IS, even at 10 K

Resistive surface layer lowers the total ceramic conductivity by one order of magnitude.

4 probe conductivity: Influence of limited reduction at grain boundaries?

$Sm_{0.1}Sr_{0.85}TiO_{3-\delta}$ ceramics :

(●) powder calcined in air (1300 °C); pressed and sintered in 5 % H_2/95% H_2 (1500 °C for 6 hrs)
(●) powder calcined in 5% H_2 (1300 °C); pressed and sintered in 5 % H_2/95% H_2 (1500 °C for 6 hrs)

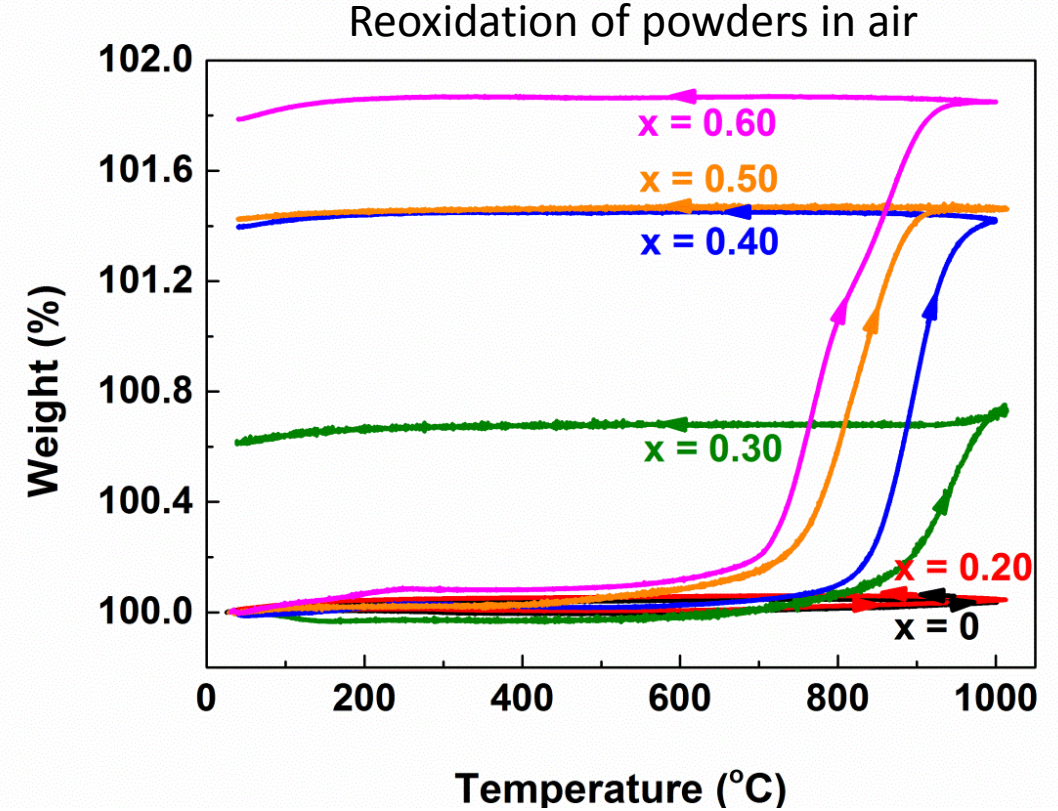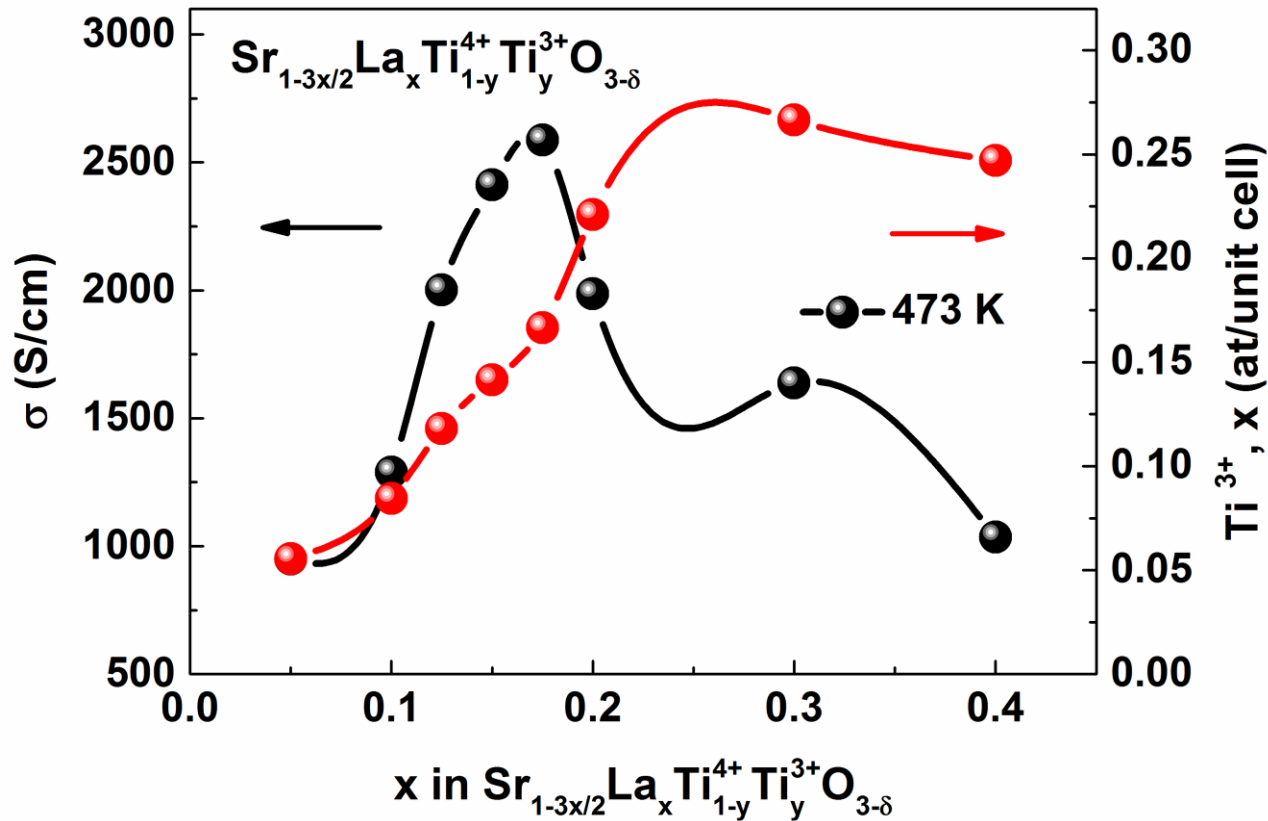$$Sr_{0.85}Sm_{0.10}TiO_3 \;+\; \delta\,H_2 \quad \rightarrow \quad Sr_{0.85}Sm_{0.10}TiO_{3-\delta} \;+\; \delta\,H_2O$$
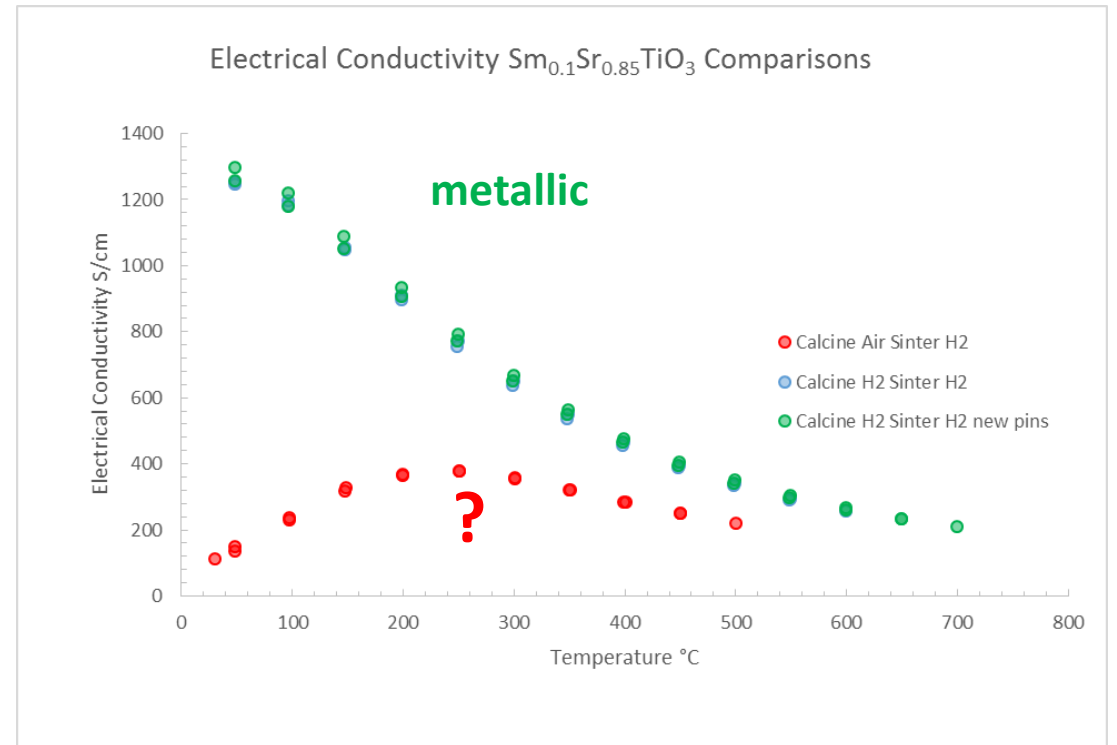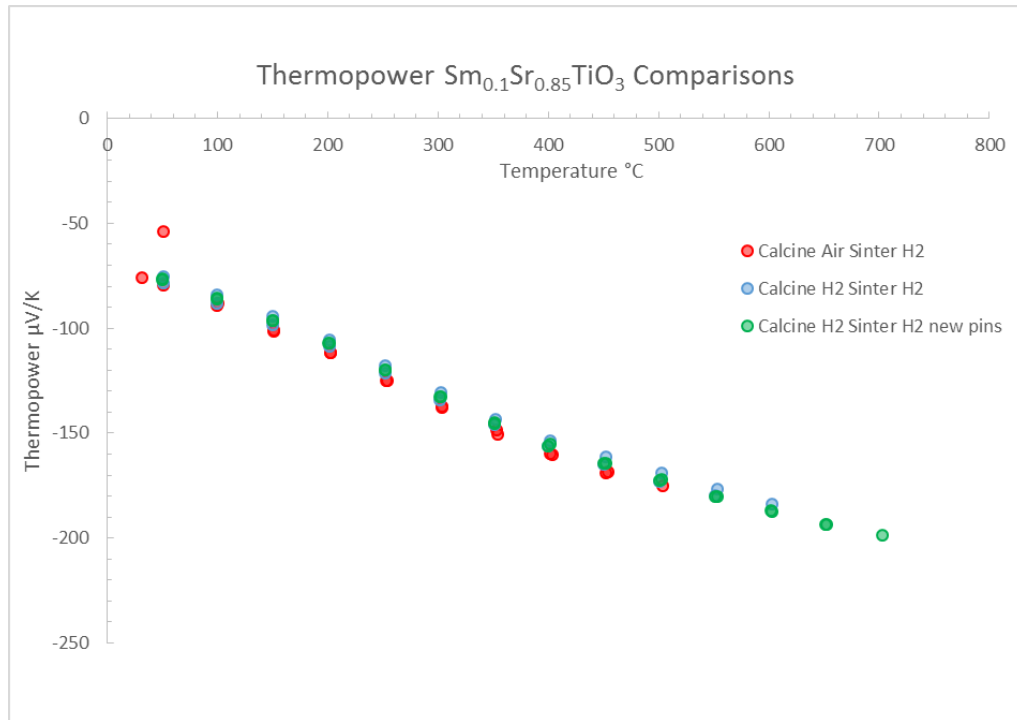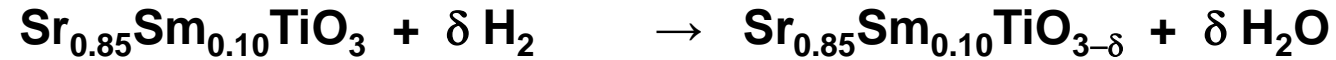
Seebeck coefficient (Thermopower) is the same for both samples
Low Temp σ is very different but high Temp σ is similar for both samples: **extrinsic effect – limited reduction/grain boundaries?**

4-probe conductivity, Ti³⁺ content and re-oxidation characteristics

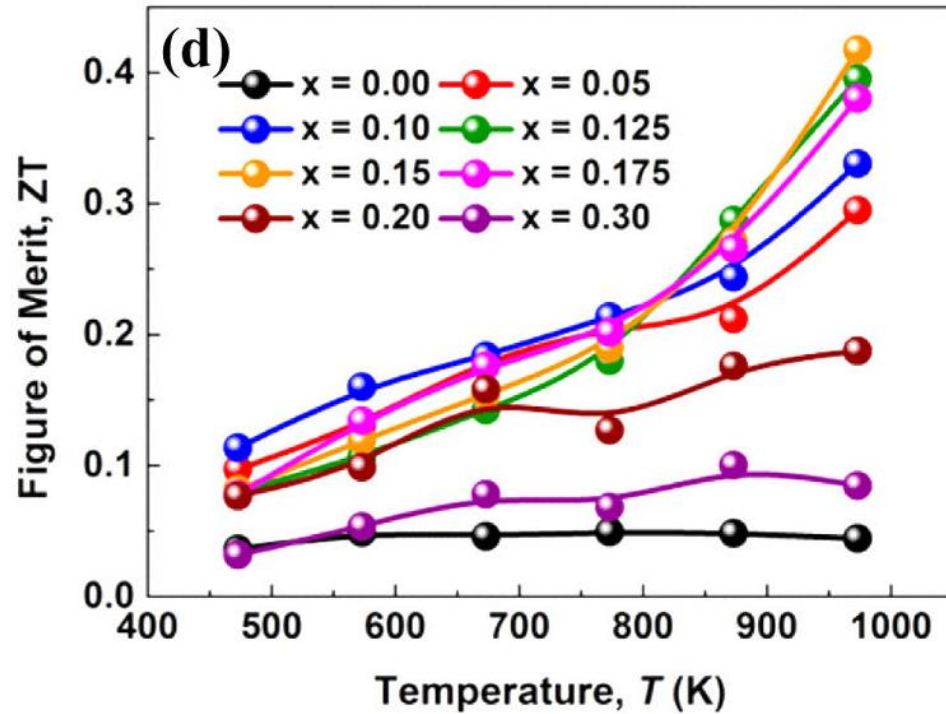**Conductivity maximum at ~ 15 % Ti³⁺**

Complex conductivity behaviour: doesn't scale simply with Ti³⁺ content

Reoxidation of samples with > 20 % Ti³⁺ is rapid

Excellent n-type thermoelectric oxides (see next presentation)

*Z Lu, H Zhang, W Lei, D.C. Sinclair and I.M. Reaney, Chem. Mater., **28** (2016) 925-935*

$Sr_{1-3x/2}La_xTiO_3$: Figure of Merit (ZT)
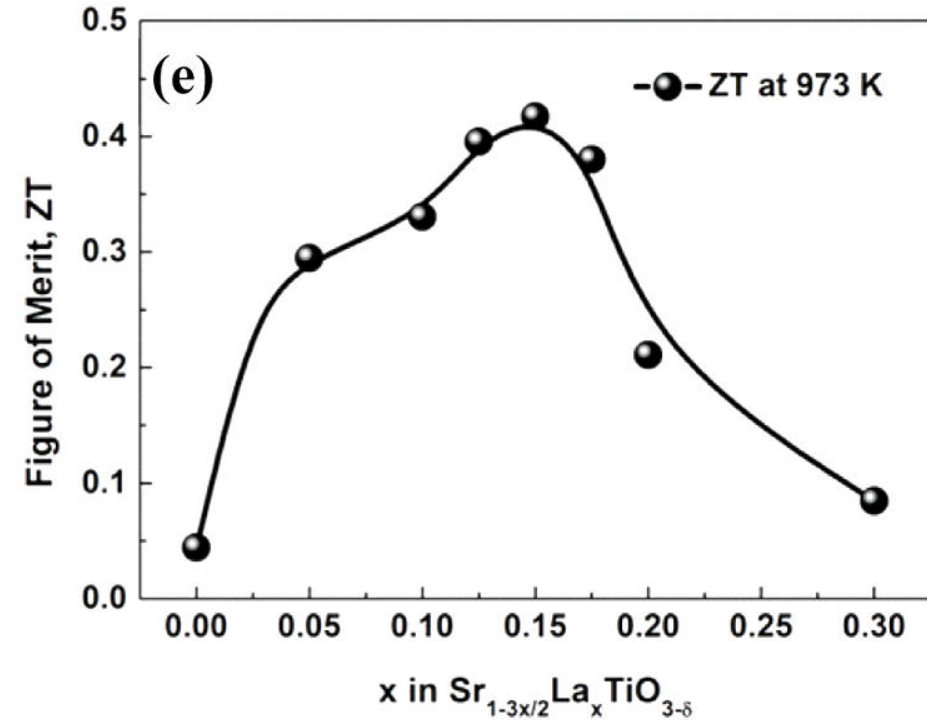
- ZT
  - Increases with increasing T
  - Increases with increasing La up to x = 0.15
 - Maximum thermoelectric properties at x = 0.15 where ZT = 0.41 at 973K

*Z Lu, H Zhang, W Lei, D.C. Sinclair and I.M. Reaney, Chem. Mater., **28** (2016) 925-935*

Synthesis & Stability of EuTiO₃ ceramics

Reaction: $Eu_2O_3 + 2TiO_2 + H_2 (g) \xrightarrow[\text{12 h}]{\text{1250 °C}} 2\ EuTiO_3 + H_2O (g)$

5 % H_2/95 % N_2 (atmosphere)
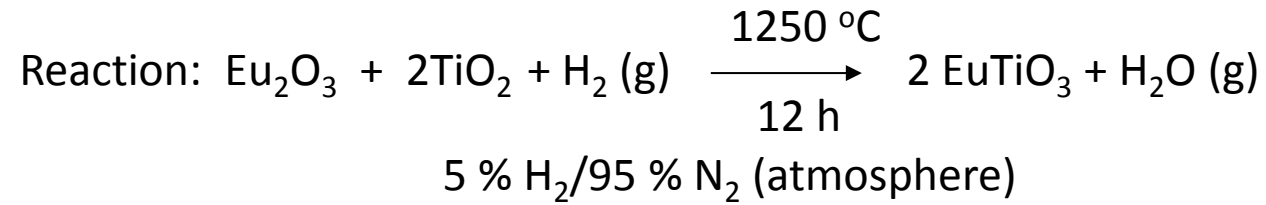
Ceramics : Sinter EuTiO₃ green bodies at 1500 °C in 5 % H_2 (g) for 6 – 18 hours

Heating/cooling rate = 5 °C/min

Annealed ceramics in Air, O_2 and N_2 at 200 °C for 24 hours
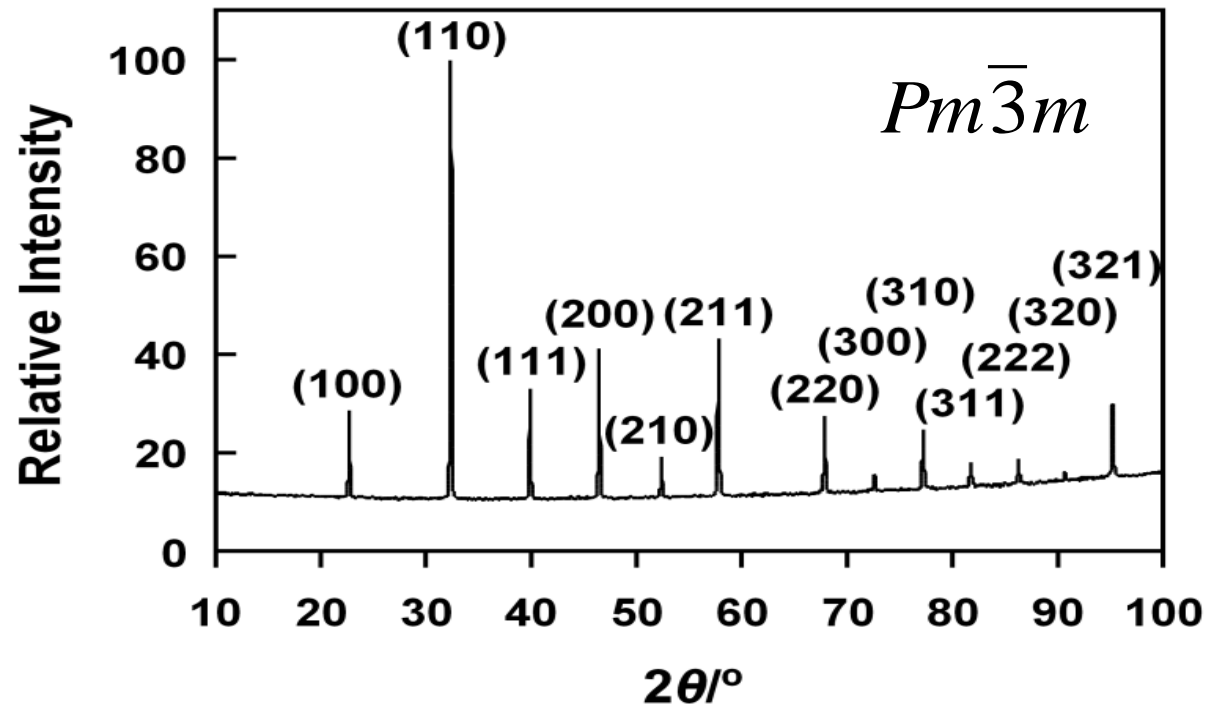
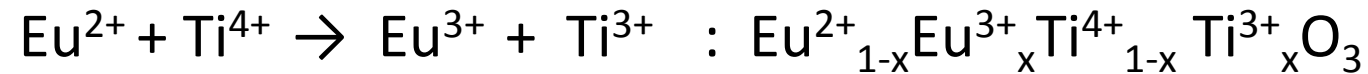## Thermogravimetric Analysis (TGA)

Crushed powder from 6 h ceramic

$Eu_2Ti_2O_7$

Eu^{3+}

Air

O_2

N_2

~ 2.9 – 3.0 %

"$EuTiO_3$"

Eu^{2+}

Weight/%

$T/°C$
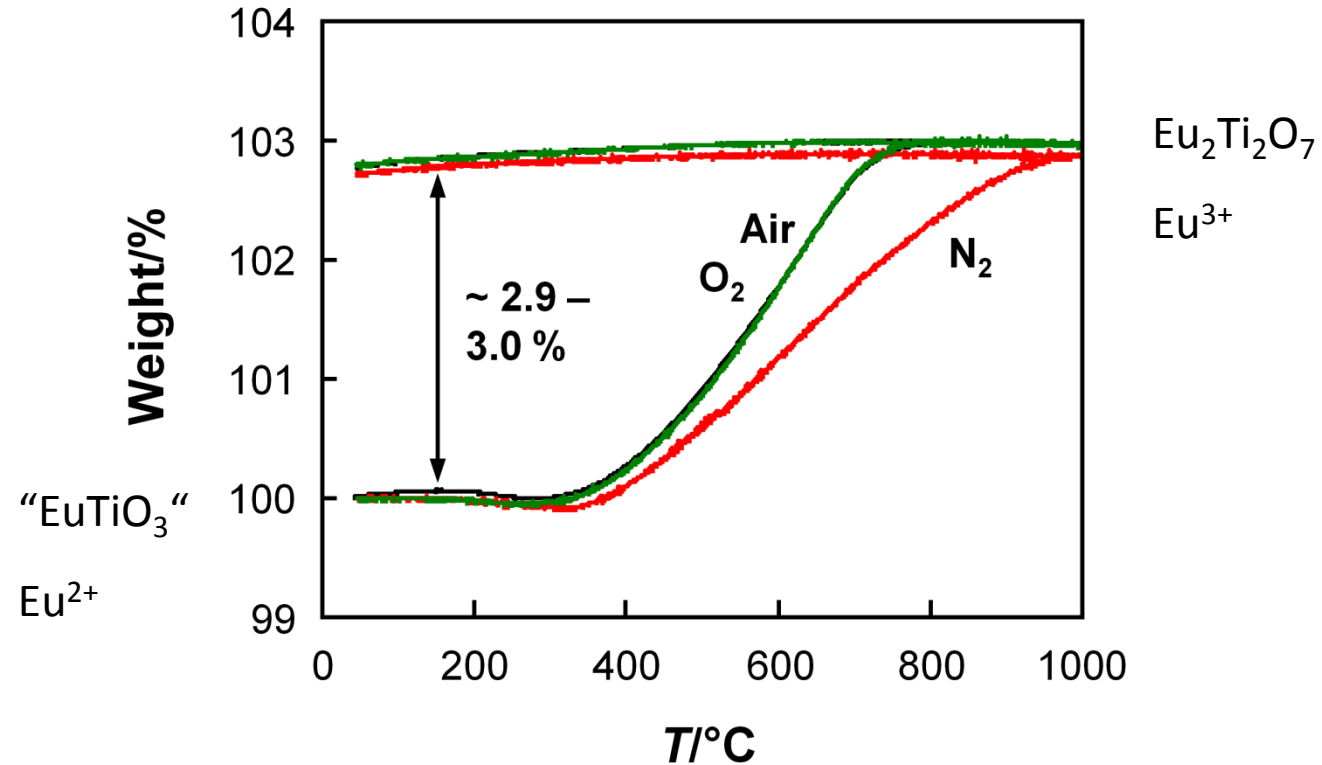
- " $EuTiO_3$ " gains weight at > 300 °C.

- Up-take of O_2 causes oxidation to $Eu_2Ti_2O_7$ ($Eu^{3+,}$ pyrochlore)   [expect ~ 3.2 %]

- No evidence for a large amount of oxygen deficiency in as-prepared "$EuTiO_3$ "

- Exposure to ppm levels of O_2 at T > 300 °C is sufficient for decomposition.

- 'Safe' working range for $EuTiO_3$ in air/N_2 is ~ 250 °C

Source of semiconductivity in 'Eu^{2+}Ti^{4+}O$_3$'

σ_b ~ 15 mScm^{-1} at 300 K : μ = 4 cm^2.V^{-1}s^{-1} : n ~ 2.3 x 10^{16} cm^{-3} at 300 K

As-prepared EuTiO$_3$ is a lightly-doped semiconductor.

(i) Oxygen-stoichiometric but with incomplete reduction of Eu^{3+}

$(\equiv$ donor doping : $\quad\quad$ Eu$^{2+} \rightarrow$ Eu^{3+} + e$^-$)

$$Eu^{2+} + Ti^{4+} \rightarrow Eu^{3+} + Ti^{3+} \quad : \quad Eu^{2+}_{1-x}Eu^{3+}_{x}Ti^{4+}_{1-x}Ti^{3+}_{x}O_3$$

(ii) Oxygen-deficient with partial reduction of Ti^{4+}

$$O^{2-} \rightarrow \tfrac{1}{2} O_2 \,(g) + 2\,e^- \quad : \quad Eu^{2+}Ti^{4+}_{1-y}Ti^{3+}_{y}O_{3-y/2}$$

or could it be (i) + (ii) ?

$$Eu^{2+}_{1-x}Eu^{3+}_{x}Ti^{4+}_{1-x-y}Ti^{3+}_{x+y}O_{3-y/2}$$
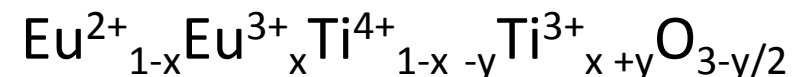
Difficult to establish mechanism (ii) via 'conventional methods such as TGA

Dense ceramics

(a) 5 μm — 6 hr sinter

(b) 20 μm — 18 hr sinter

M'' FWHM = 1.4 decades

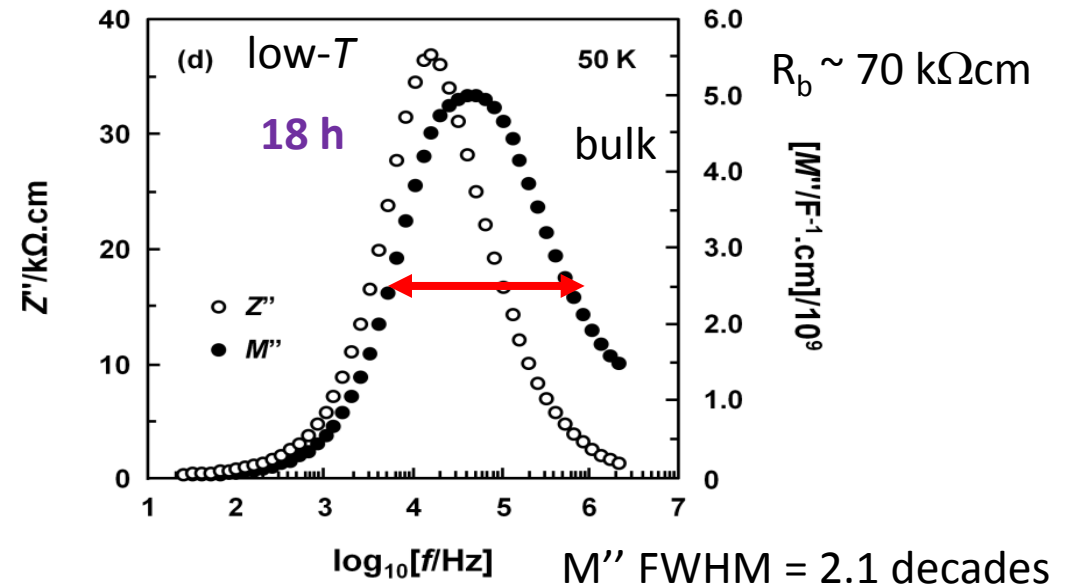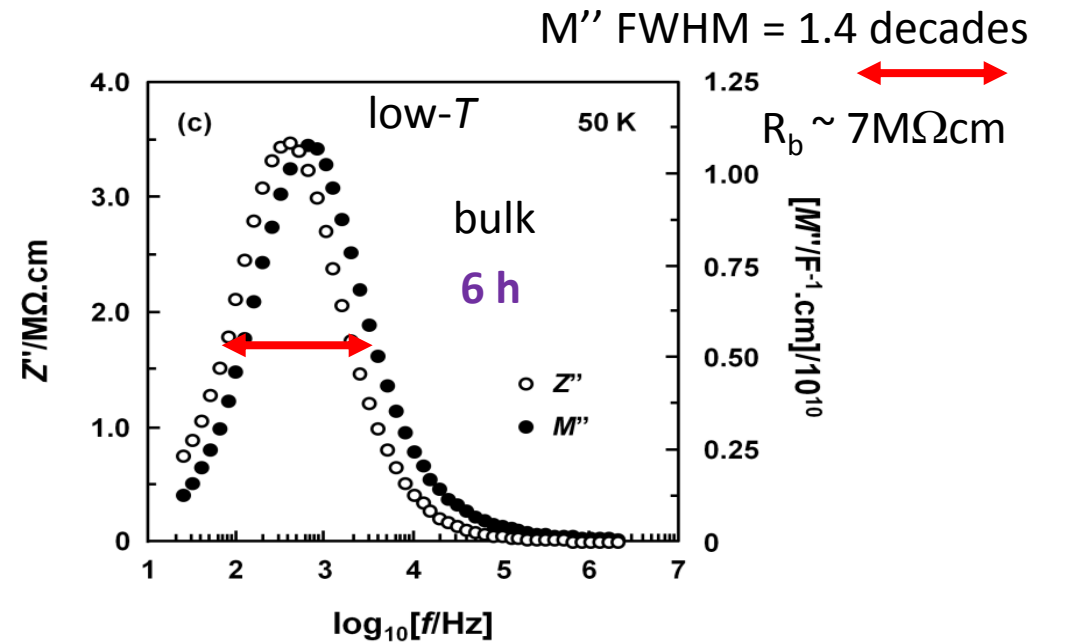$R_b \sim 7 M\Omega cm$

$R_b \sim 70 k\Omega cm$

M'' FWHM = 2.1 decades
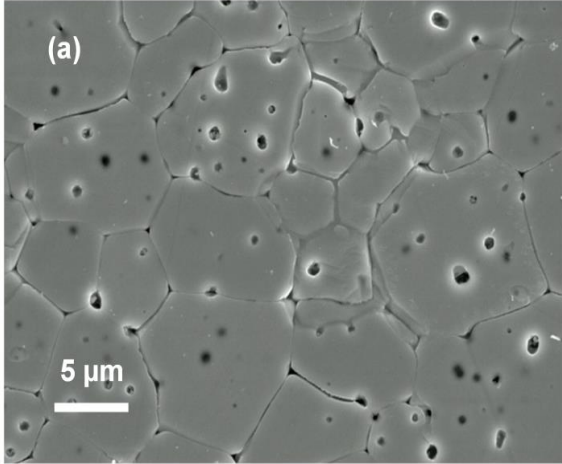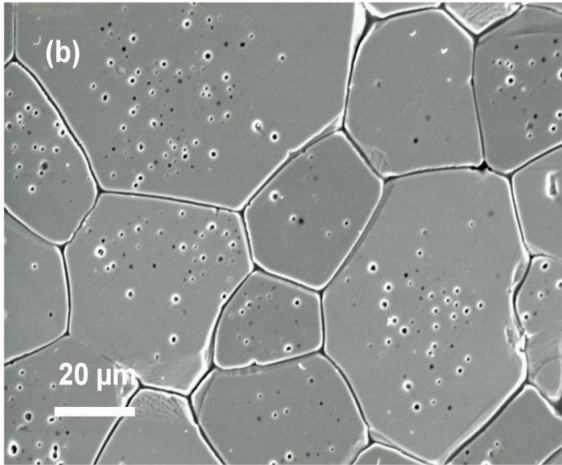
Grain growth increases with sintering time

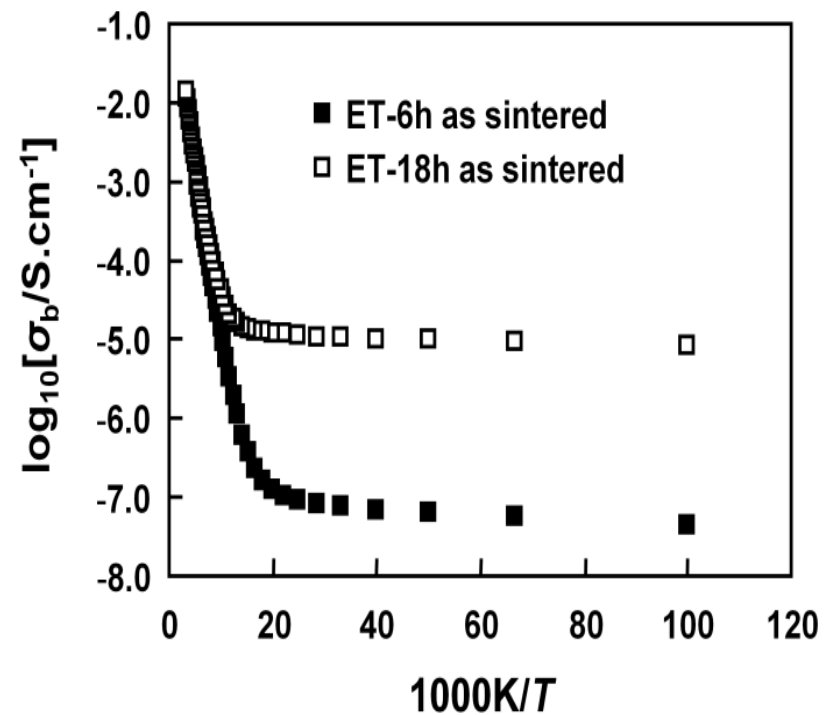• Both ceramics are heterogeneous : R_b is similar for T > 100 K

BUT

below 100 K 18 hr sinter is more conductive and grains are more heterogeneous
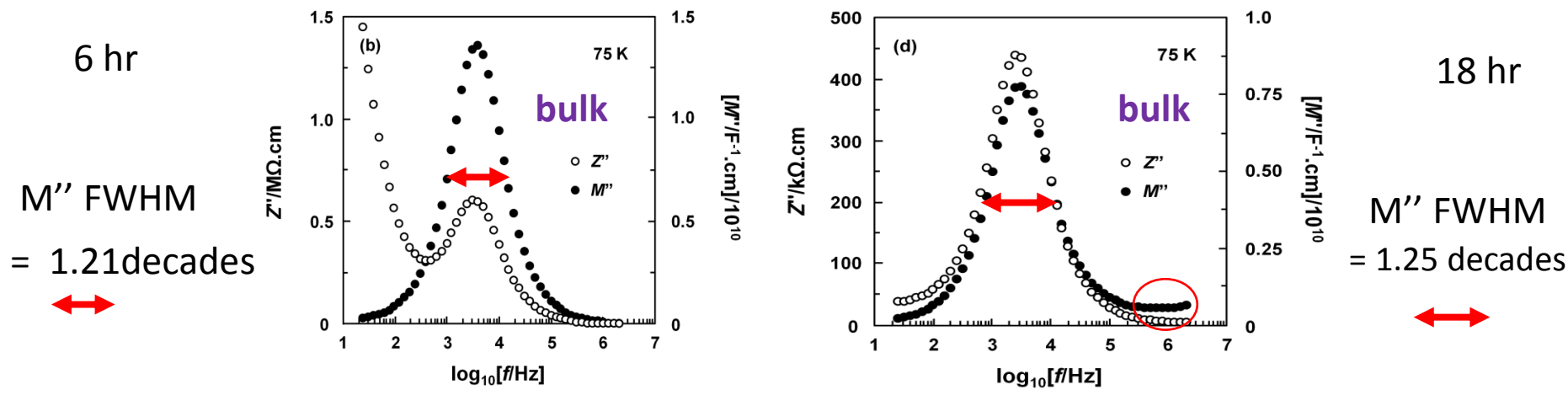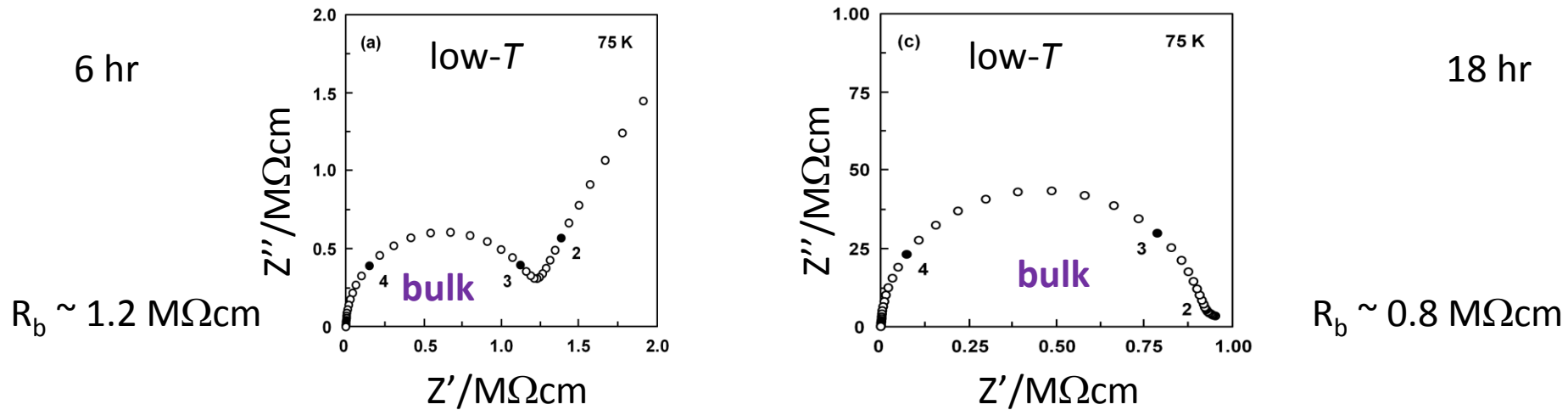
Bulk conductivity = $1/R_b$

Two regions.

(High- *T*) 100 - 300 K Ea ~ 80 meV

R_b (6 h) ~ R_b(18 h)

(Low-*T*) 10 - 100 K   Ea ~ 0 eV

R_b (18 h) << R_b (6 h)

Annealed ceramics at 200 °C (air, O_2, N_2, 5 % H_2/95 % N_2)

6 hr

R_b ~ 1.2 MΩcm

18 hr

R_b ~ 0.8 MΩcm

6 hr

M'' FWHM = 1.21 decades

18 hr

M'' FWHM = 1.25 decades

R_b is resistive and grains are electrically homogeneous

R_b is resistive but grains show evidence of electrical heterogeneity
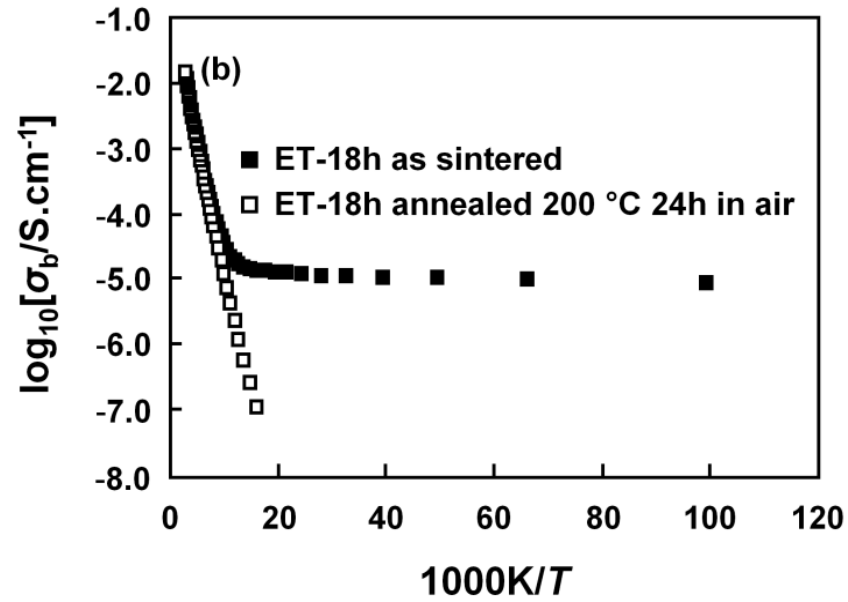
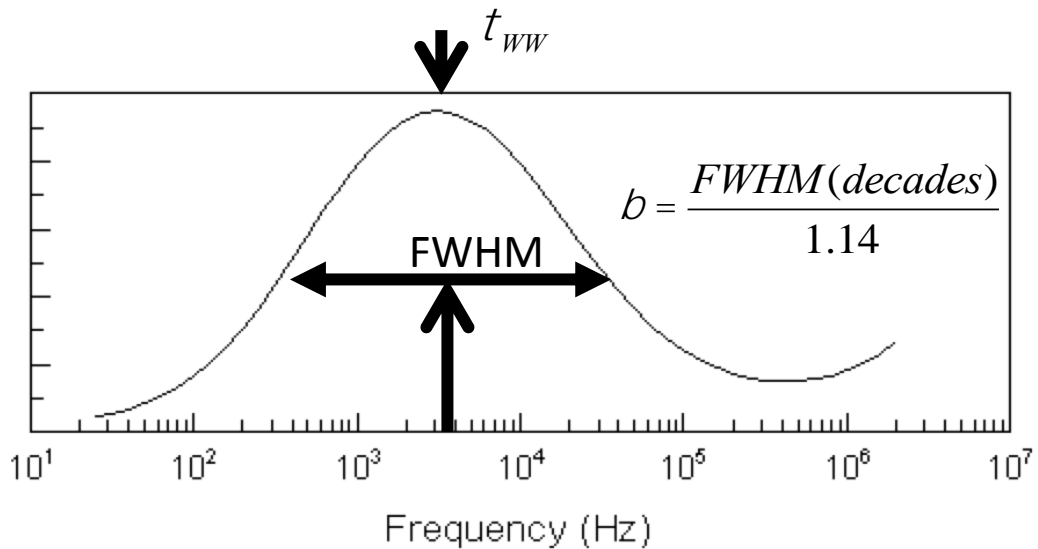# Sintered v's Annealed Ceramics

Bulk conductivity

6 hr
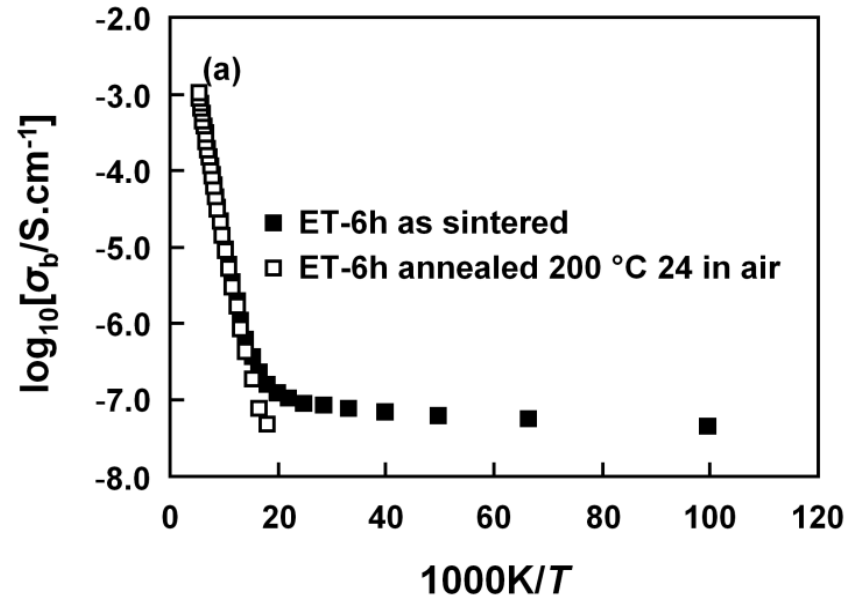
Annealing at 200 ^oC removes the low T conductive state for both samples.

18 hr

This annealing is ~ 100 ^oC below the decomposition temperature.

Non ideal behaviour

$$f(t) = \exp\left[-\left(\frac{t}{t_{WW}}\right)^{b}\right] = \frac{1}{n}\sum_{i=0}^{n}\exp\left(\frac{-t}{t_i}\right)$$

The non-exponential conductivity relaxation can be described by a Kohlrausch–Williams–Watts (KWW) function φ(t), which represents the distribution of relaxation times

The peak gives the average τ and the FWHM over 1.14 decades gives beta

EuTiO$_3$ sintered at 1500 ^{o}C for 6h in 5 % H$_2$
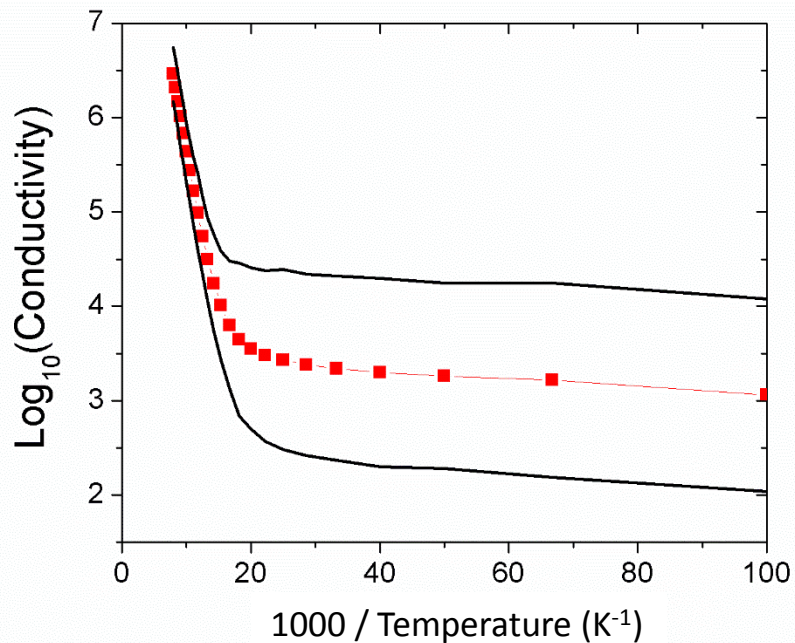
EuTiO$_3$ sintered at 1500 ^{o}C for 6h in 5 % H$_2$ and annealed at 200 ^{o}C for 24h in Air
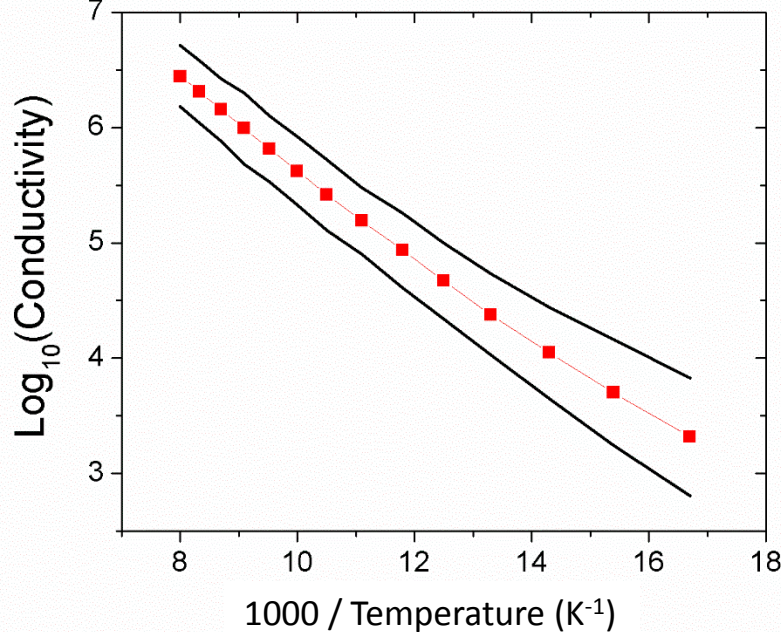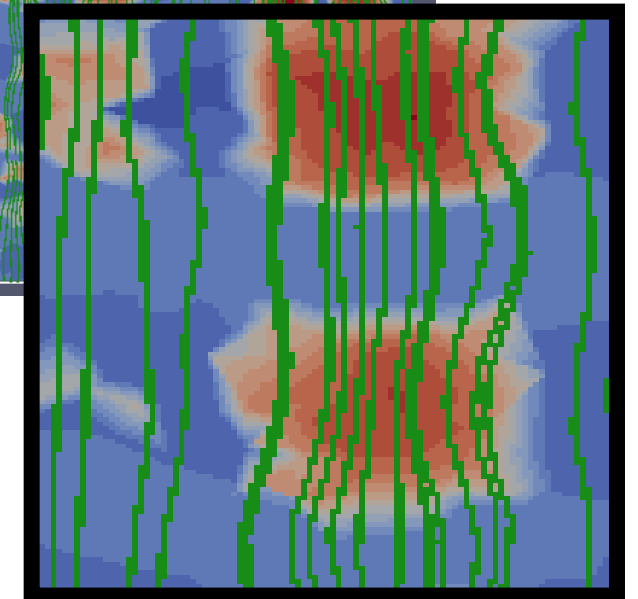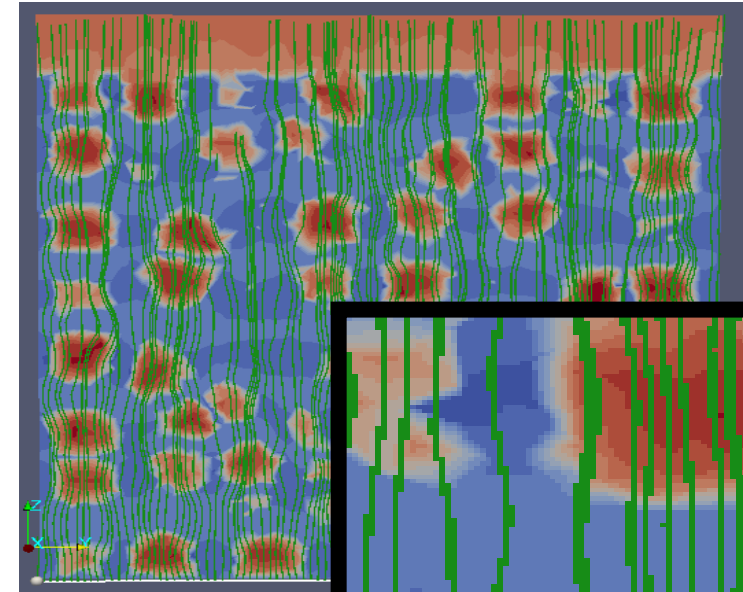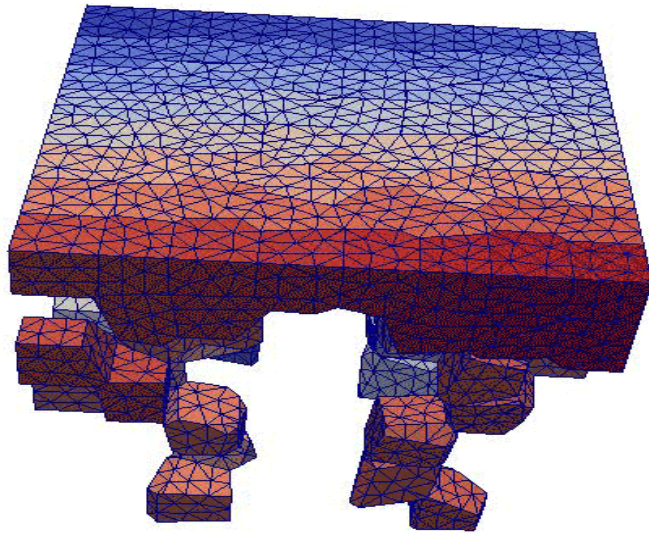
Finite Element modelling at Sheffield (Julian Dean)

The electrical microstructure lead to paths which are more favourable

Electrical response primarily made of these, with small contributions from parallel ones

In some cases (e.g. 10% change in resistance) only 50% of the grains make up the observed response!

Conclusions

- **La donor-doping in BaTiO$_3$: A site doping with B-site vacancies (ionic compensation)**

  The semiconductivity in La-doped air-fired samples and the ptcr effect is linked to oxygen loss related to the presence of V$_{Ti}$.

- **La-doping in SrTiO$_3$: A-site, B-site vacancies and electronic compensation are all possible.**

  A-site vacancy samples have the highest σ of all samples processed in air and in 5 %H$_2$ and are excellent n-type thermoelectric oxides

- **EuTiO$_3$: High levels of intra & inter grain heterogeneity can result in anomalous temperature independent σ at low T.**

  There are some unusual low temperature conduction mechanisms in reduced perovskite-type titanates