Defect Engineering Strategies in Energy and Electronic Materials

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Outline

- Research aims
- Motivation
- Defects in Ge
- Nuclear Hydrogen Production
- Modelling of Nuclear Materials
- Modelling of SOFC & SOEC
- Genetics of Superionic Conductivity
- Future Perspectives: Anomaly Detection
- Summary

Research Aims

- **Group:** Alex Chroneos (Prof.), Stavros-Richard Christopoulos & Nikos Kelaidis (postdocs) & 4 PhD students,Stratis Kanarachos (Reader), David Parfitt (SL),
- **Applied modeling**: the simulations are used to interpret, guide and support experimental studies.
- **Techniques:** 1) Atomistic modeling (density functional theory, molecular dynamics) and 2) advanced methods (machine learning, genetic algorithms etc) 3) Experiment.
- Range of systems studied (particularly oxides & semiconductors).
- Technologically important systems. Focus on energy applications (fuel cell, solar cell & nuclear materials).

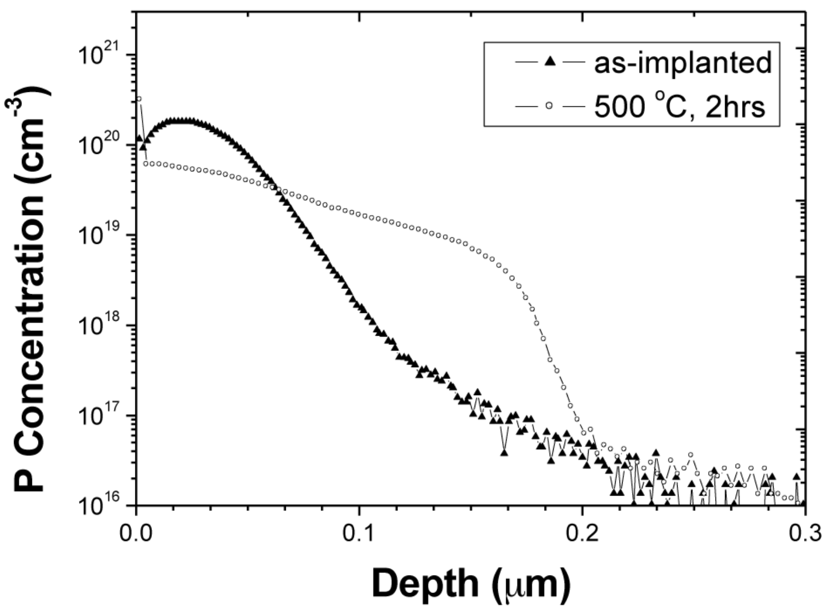
Motivation

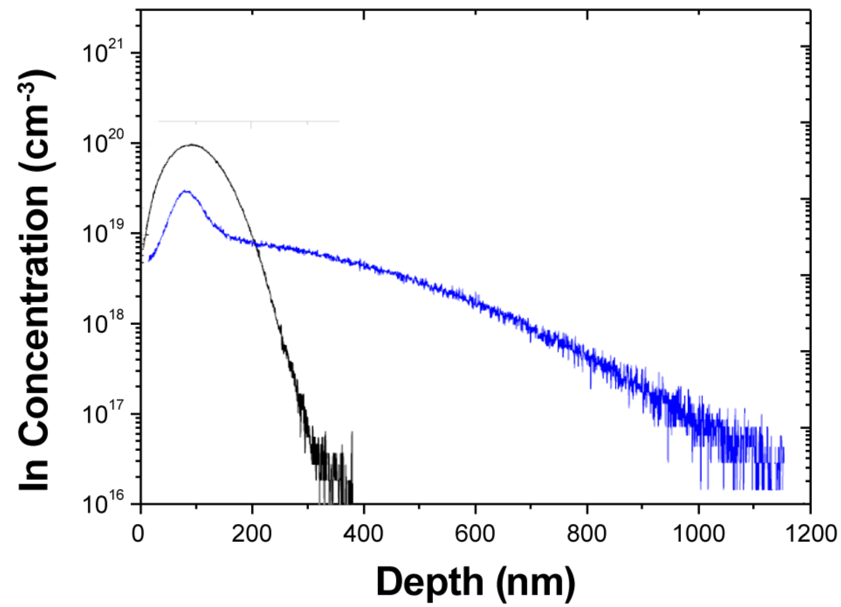
- Ge was abandoned due to the unstable Ge oxide. Si prevailed.
- high-*k* dielectrics eliminated the need for a stable native oxide.
- Ge, SiGe: higher carrier mobilities compared to Si.
- Relative compatibility with Si processes.

- **Aims:** To calculate the stability and diffusion of impurities in Ge.

Ge used in the first transistor (1947, Shockley, Bardeen, Brattain)

Defects in Ge





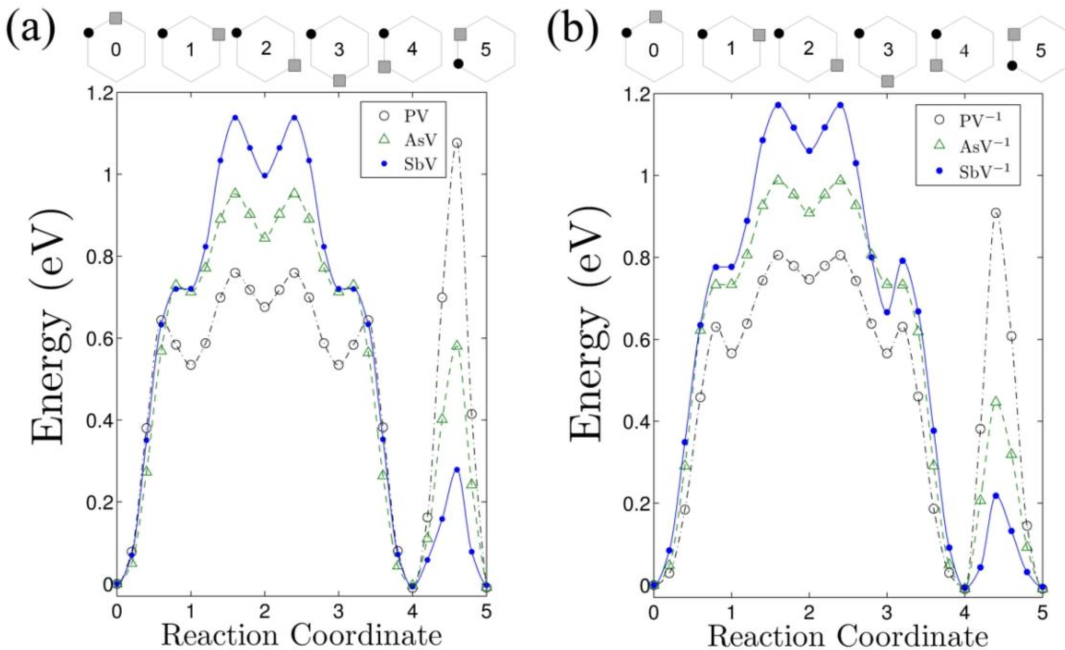
In Ge two issues:

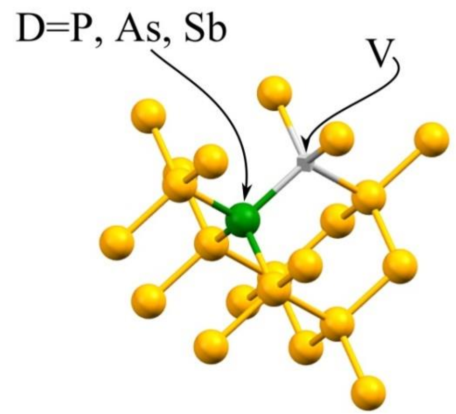
- Fast donor atom (P, As, Sb) diffusion via vacancies. Problem: cannot contain dopants in defined regions.
- Dopant atom clustering leads to electrical deactivation.

Chroneos *et al.* Mater. Sci. Semicond. Proc. **9**, 640 (2006).

Chroneos *et al.* J. Appl. Phys. **106**, 063534 (2009).

Defects in Ge



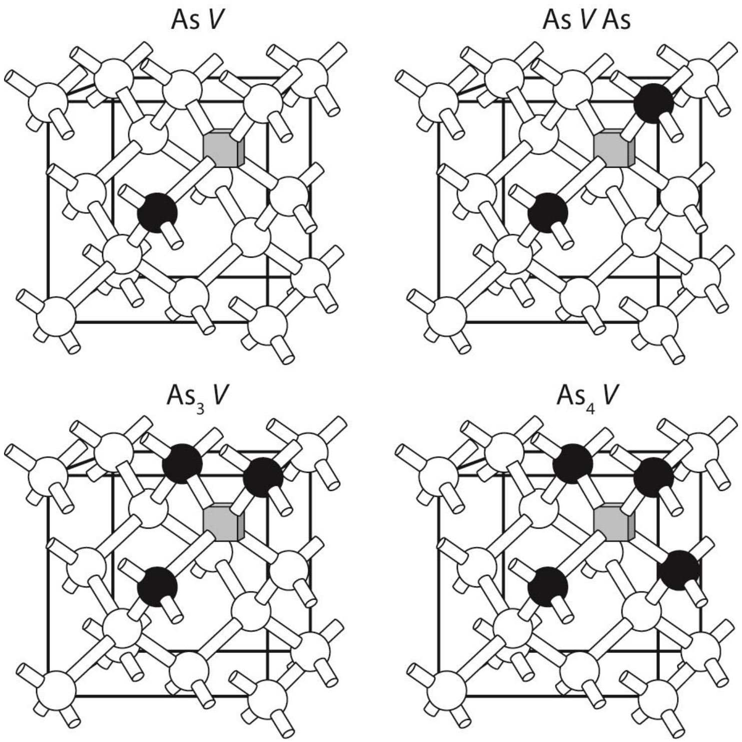


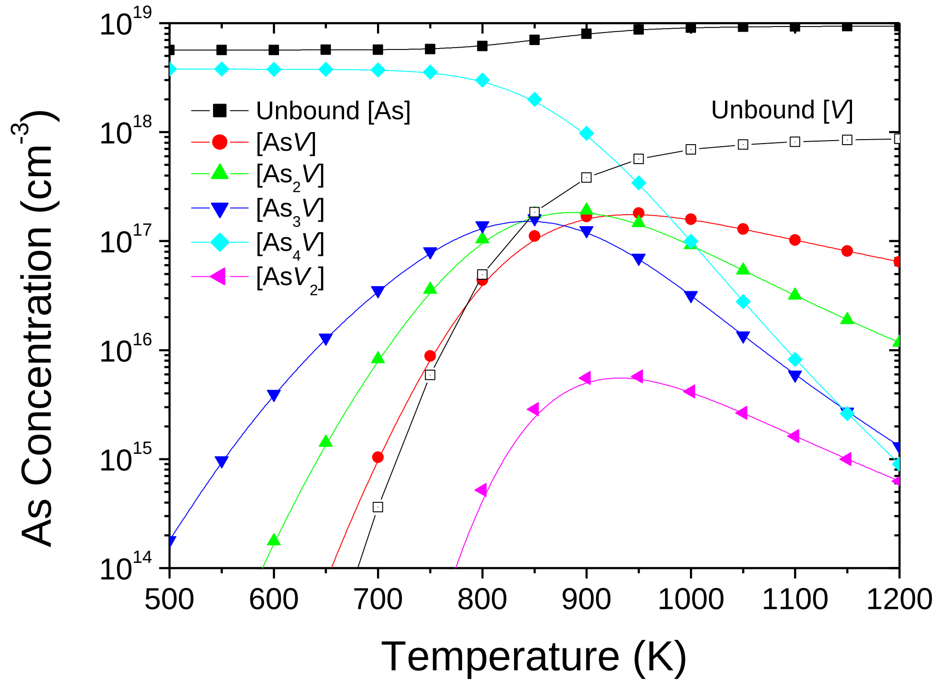
E-centre: A vacancy paired to an *n*-dopant atoms (P, As or Sb).

- The diffusion of the different *n*-type dopants (P, As, Sb) via the ring mechanism. (a) Neutral D*V* pairs, (b) singly negatively D*V* pairs.

Tahini *et al.* Appl. Phys. Lett. **99**, 072112 (2011).

Defects in Ge



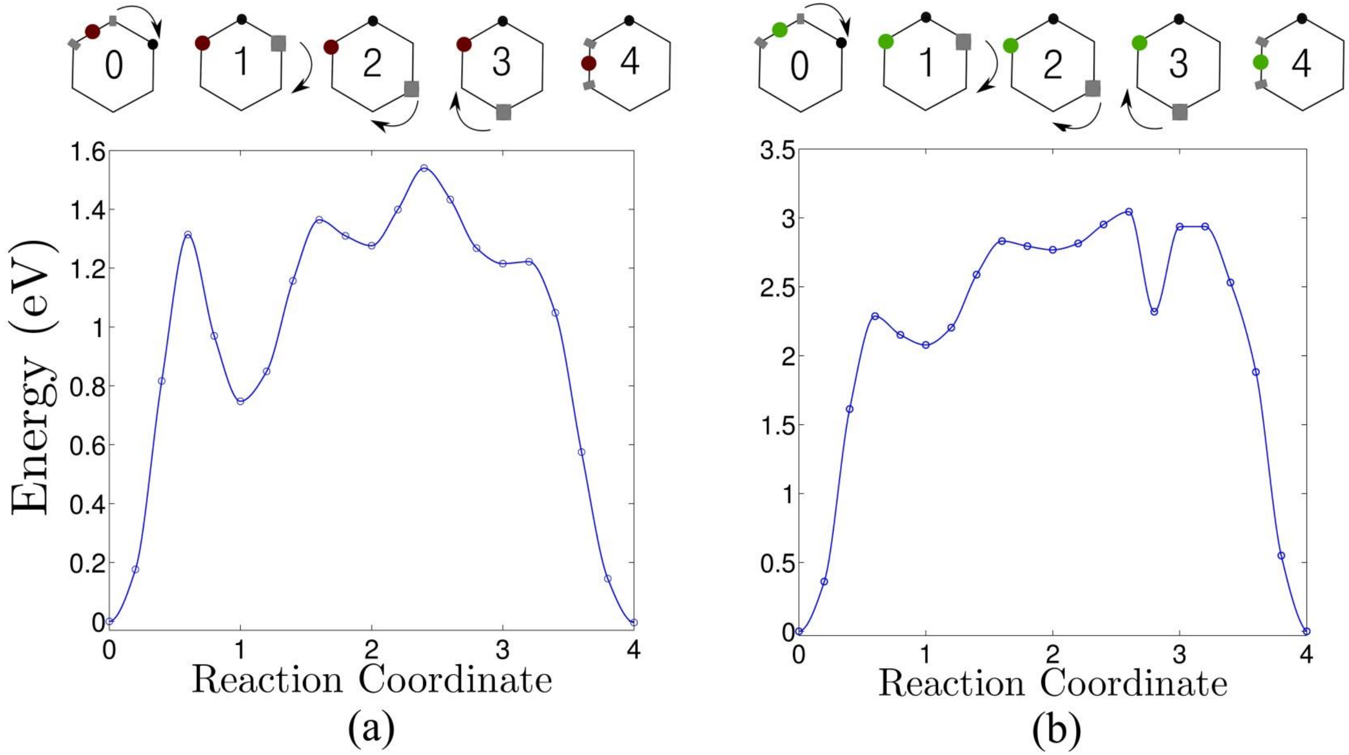


- Stable clusters with up to 4 As around a *V*.
- Impact on activation, diffusion of As in Ge.

$$\frac{[\mathrm{As}_n V]}{[\mathrm{As}]^n [V]} = \exp\left(\frac{-E_b(\mathrm{As}_n V)}{k_B T}\right)$$

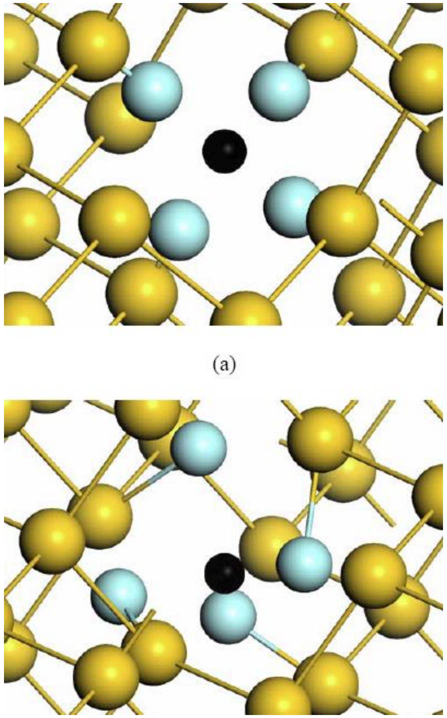
Chroneos *et al.* Appl. Phys. Lett. **91**, 192106 (2007); Phys. Rev. B **77**, 235208 (2008).

Defects in Ge

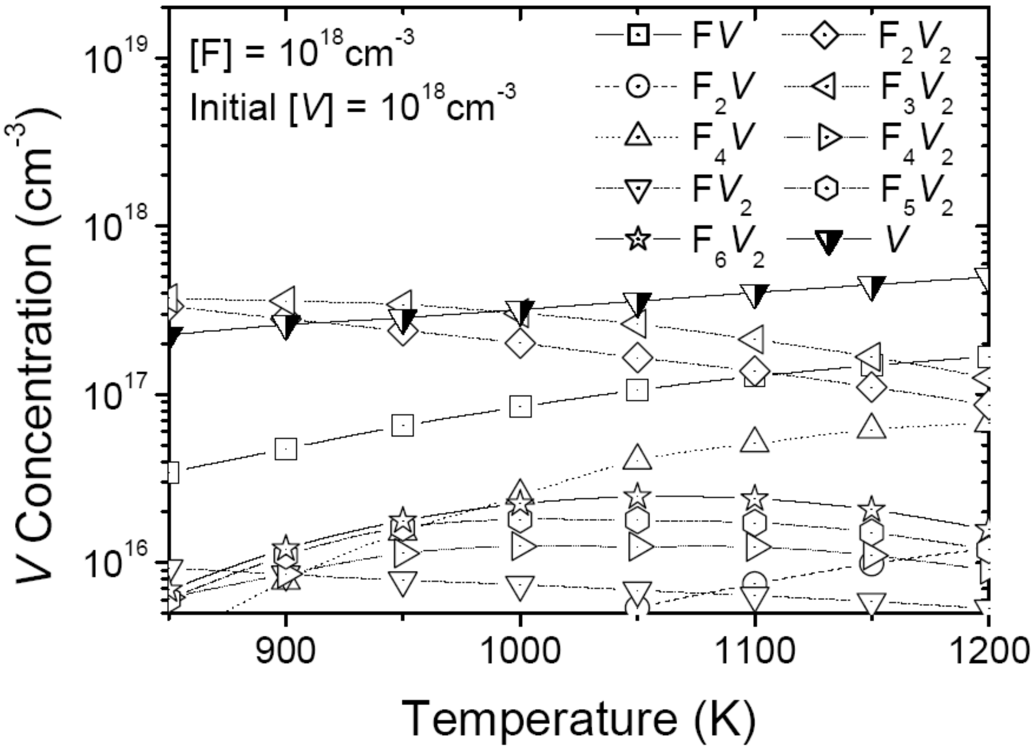


Isovalent codoping? Diffusion path of the P*V* pairs in the presence of (a) Sn and (b) Hf. On the top of the figures is the ring mechanism of diffusion for the P*V* pair in the presence of Sn and Hf. **Migration barriers increase significantly.**

Defects in Ge



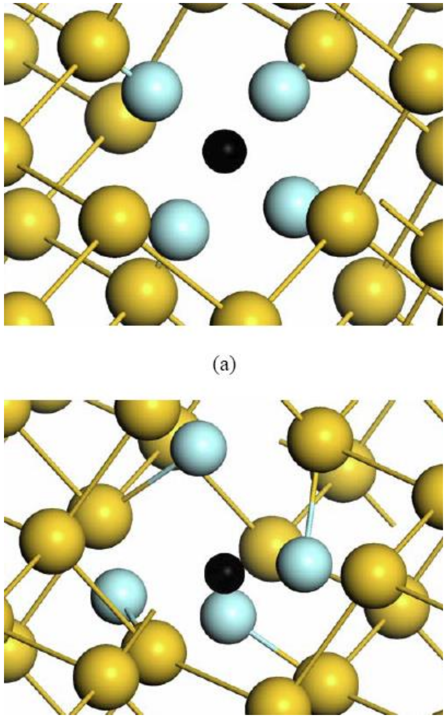
(a)

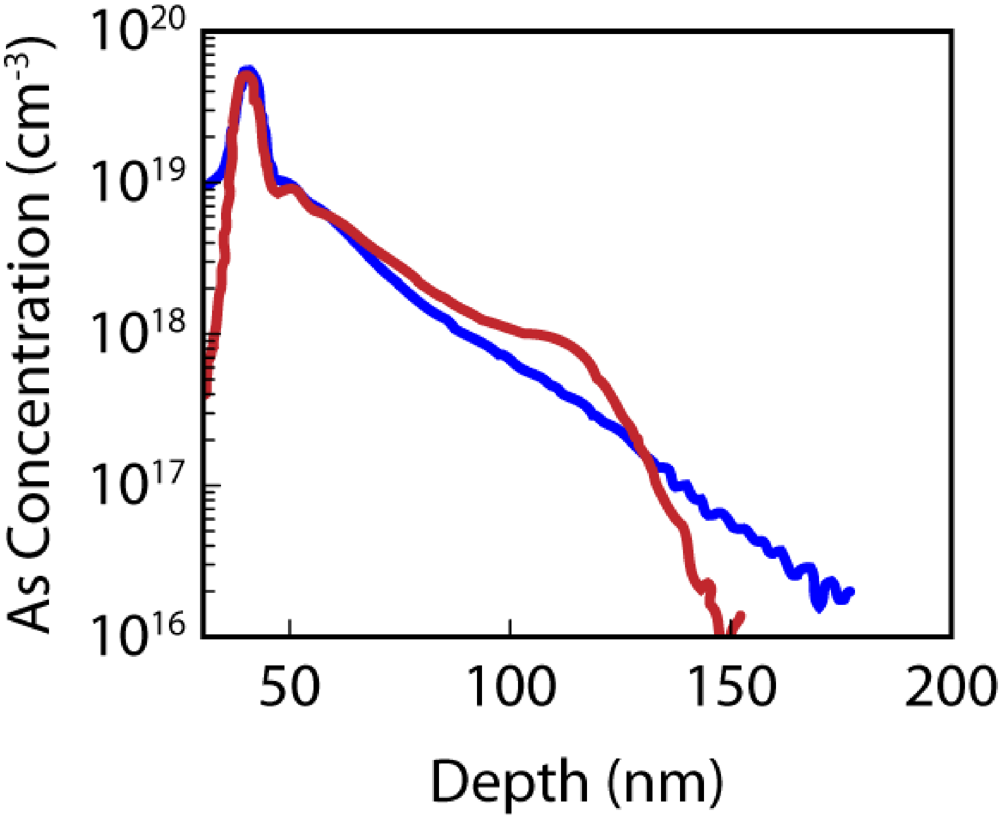


- $nF + mV \rightarrow F_nV_m$
- Vacancies need to be controlled.
- F doping leads to control of the dangling bonds hence the vacancies.

Chroneos *et al.* J. Appl. Phys. **106**, 063707 (2009).

Defects in Ge



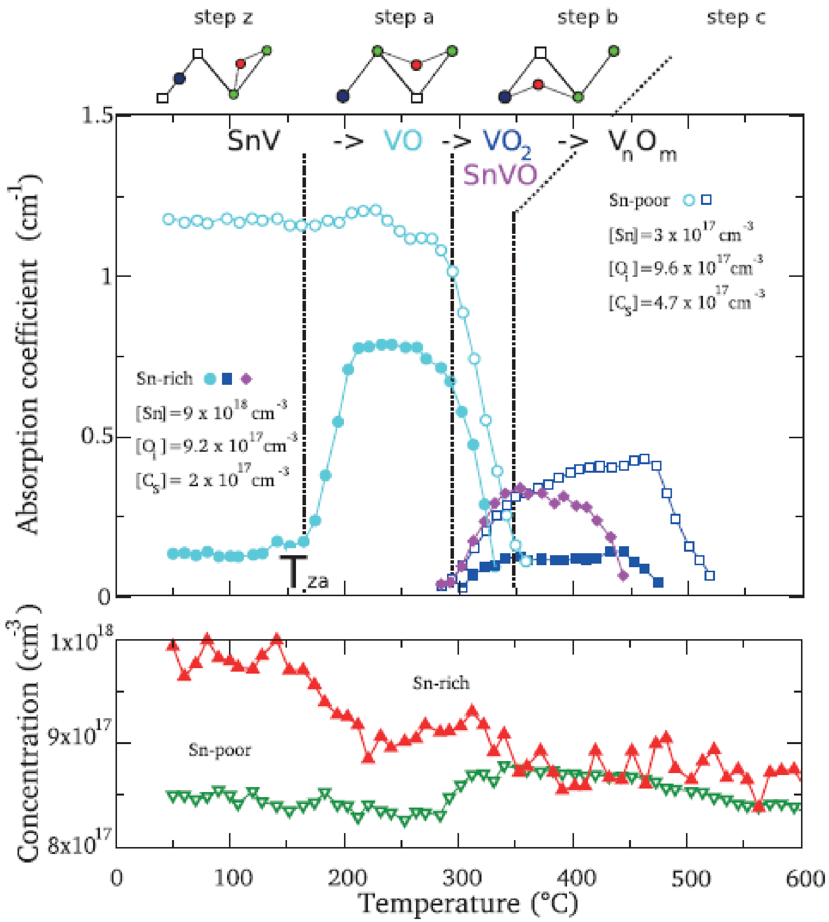


- $nF + mV \rightarrow F_nV_m$
- Need to control the vacancies?
- Solution: codoping with F as it saturates the dangling bonds.

Impellizzeri, Chroneos *et al.* J. Appl. Phys. **109**, 113527 (2011).

Si for Photovoltaics

- Si is important for photovoltaic applications.
- Control of oxygen, carbon and point defects is important to improve properties.
- Use of DFT in conjunction with experiment (IR spectroscopy) to investigate the formation and evolution of oxygen-vacancy clusters.
- Propose defect engineering strategies involving Sn, Pb and Hf to control the formation of clusters.



Chroneos *et al.* Appl. Phys. Lett. **99**, 241901 (2011).

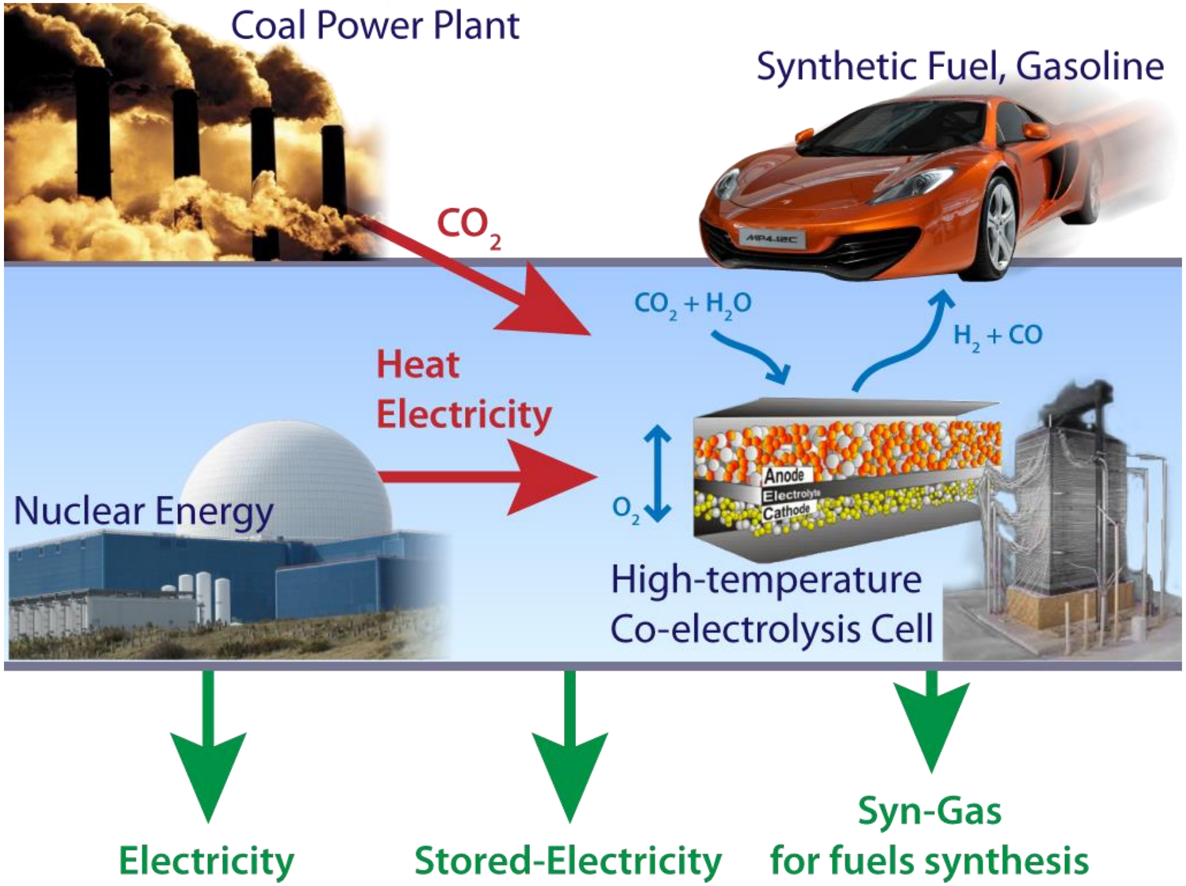
Motivation

- Emissions reduction through carbon neutral technologies.
- Increasing worldwide energy demand.
- Finite resources of fossil fuels.
- Active research interest on renewables and nuclear energy.
- Sustainable production of H? Need solution for SOFC, batteries, novel structural materials etc.

Nuclear Hydrogen Production

- Sustainable, uninterrupted and adequate supply of energy required in industrialized societies.
- The trend is increased energy consumption due to population growth or due to per capita increase in consumption because of life style changes.
- Need to develop sustainable energy sources such a renewable energy, nuclear energy and hydrogen production.
- **Challenges of the hydrogen economy:**
- Realization of the inexpensive and sustainable production of hydrogen.
- Efficient storage of hydrogen.
- Reliability of solid oxide fuel cells.
- Safety issues: considering the large scale use and storage of hydrogen.

Nuclear Hydrogen Production



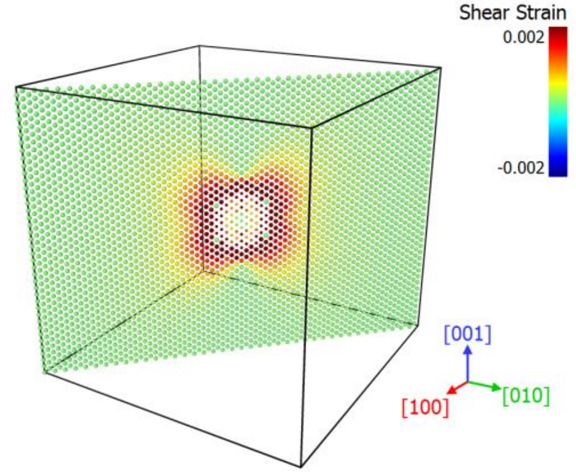
- **Nuclear hydrogen:** in essence thermochemical cycles using the heat from nuclear reactors are utilized to produce hydrogen by H_2O splitting through a solid oxide electrolyte cell (SOEC).

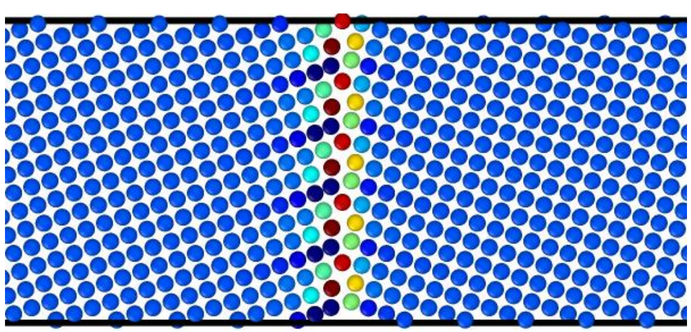
Modelling of Nuclear Materials

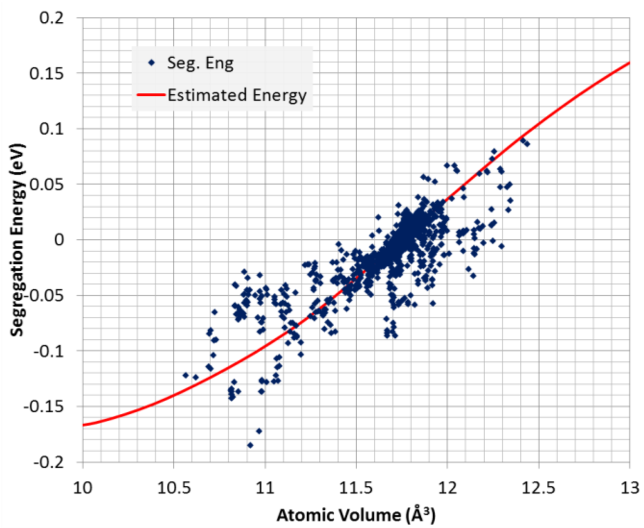
- Work on irradiation and thermal ageing mechanisms in low-alloy steel structural components.

- Studies performed in collaboration with Rolls-Royce support lifetime extension of civil US nuclear power plants. Collaboration with Westinghouse.

- Materials properties using Machine learning (in collaboration with Purdue University).







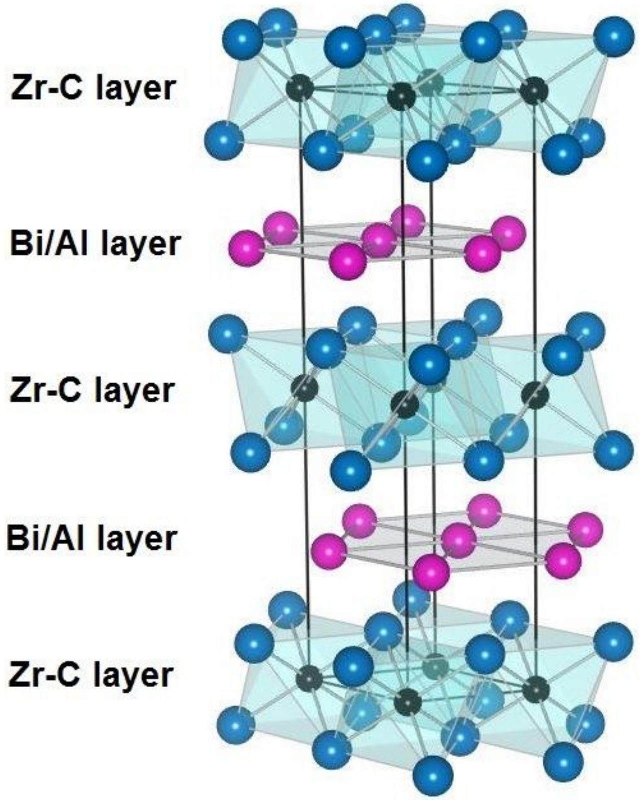
Modelling of Nuclear Materials

- In a Loss-of-Cooling Accident (Fukushima) it is impossibility to temper the reactor temperature as Zr clads can react over about 1200 ^{o}C with residual steam to produce H_2, leading to the release of the nuclear fuel in the reactor and to explosions.

- Protecting the fuel clad can postpone the catalytic reaction and protect the nuclear fuel clad against high-temperature oxidation.

- Synthesis and computational investigation of novel ceramics.

- Discovery of new carbides extending the MAX phase family.

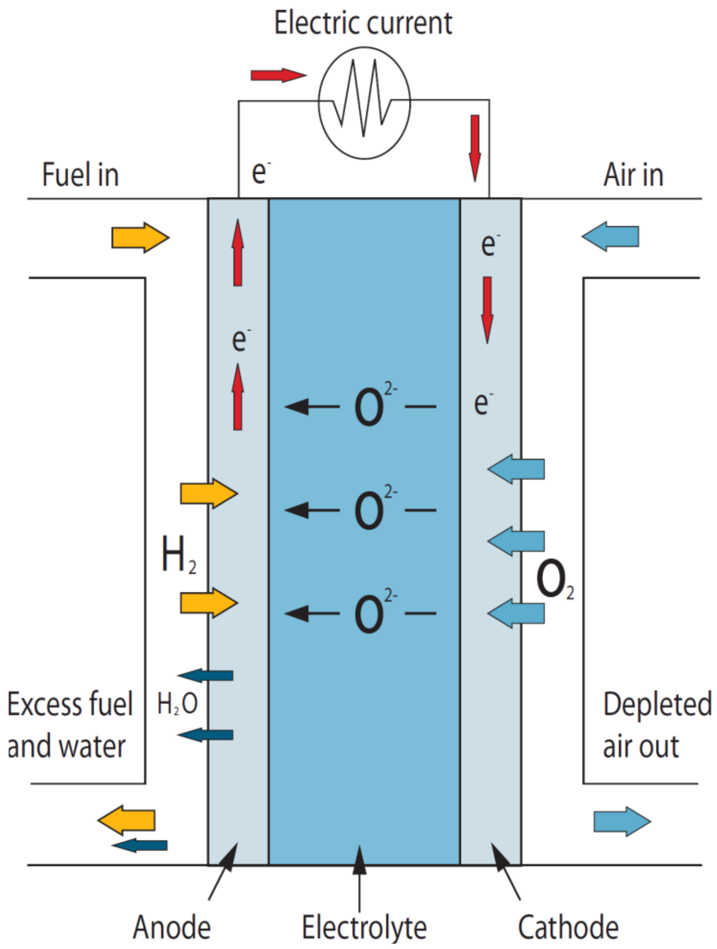


Horlait, Chroneos *et al.* Scientific Reports **6**, 18829 (2016).

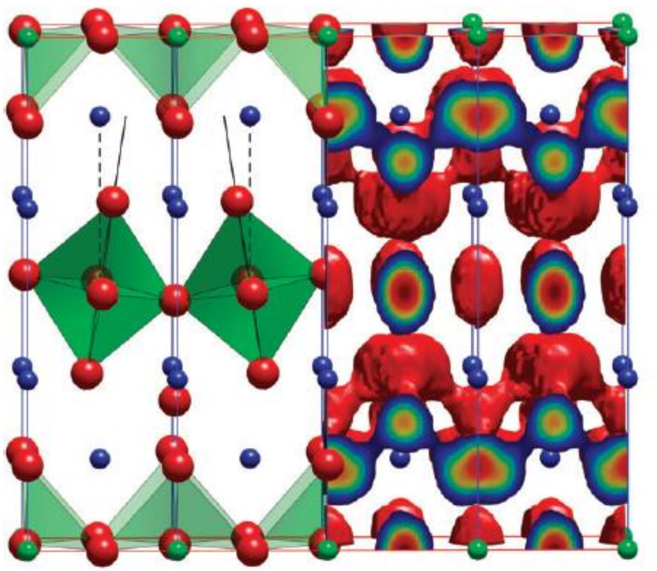
Modelling of SOFC & SOEC

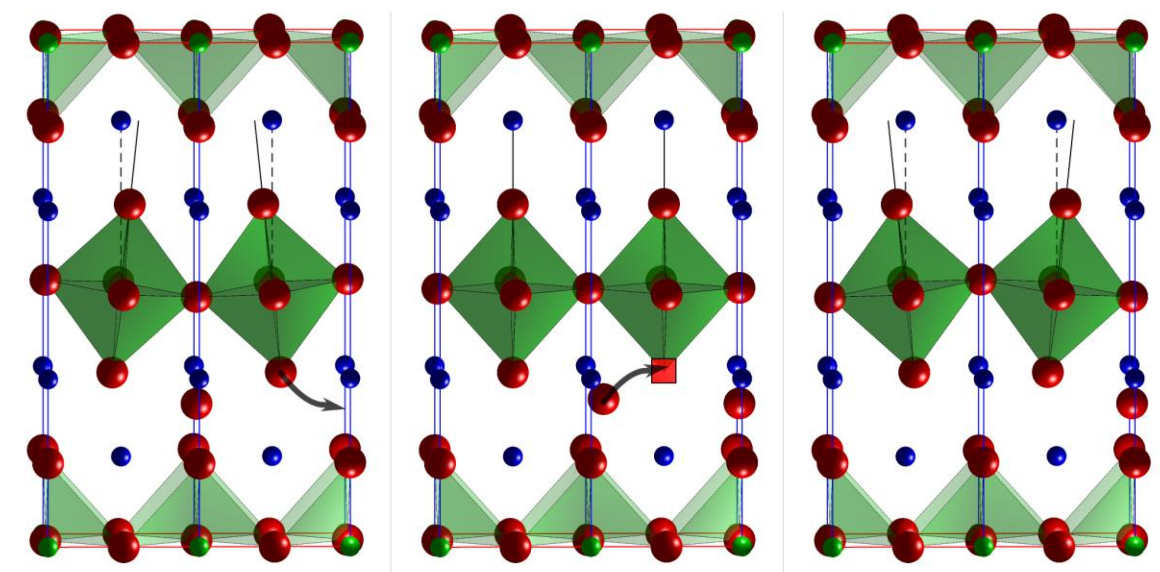
Motivation: Lower T of operation in SOFC & SOEC.

- Need materials with good electrochemical, catalytic properties and good thermal and mechanical stability.
- Perovskite-related materials are important candidates for IT-SOFC were enhanced oxygen diffusion is required.
- **Case study:** Investigate oxygen self-diffusion using simulation to predict the mechanism and activation energy of migration.



Modelling of SOFC & SOEC

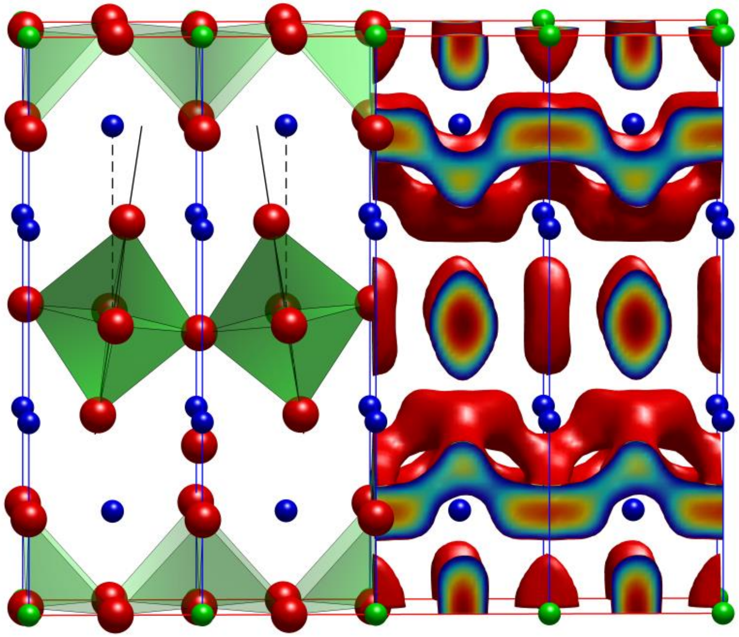


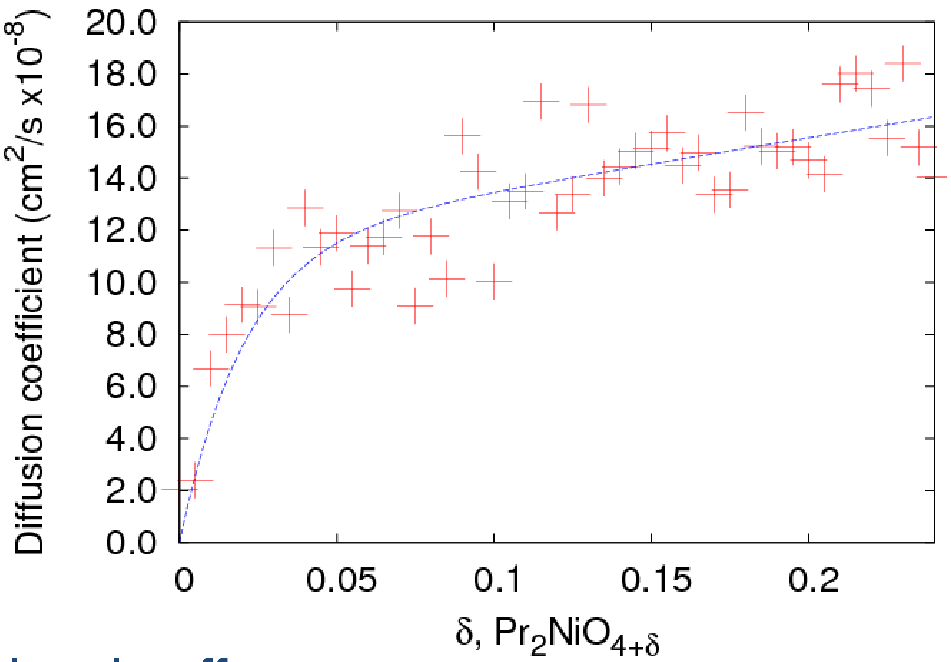


- Ruddlesden-Popper Series ($A_{n+1}B_nO_{3n+1}$) such as $La_2CoO_{4+\delta}$.
- Employ molecular dynamics and/or density functional theory.
- Good agreement between MD + DFT results.

Chroneos *et al.* J. Mater. Chem. **20**, 266 (2010); Phys. Chem. Chem. Phys. **12**, 6834 (2010).

Modelling of SOFC & SOEC

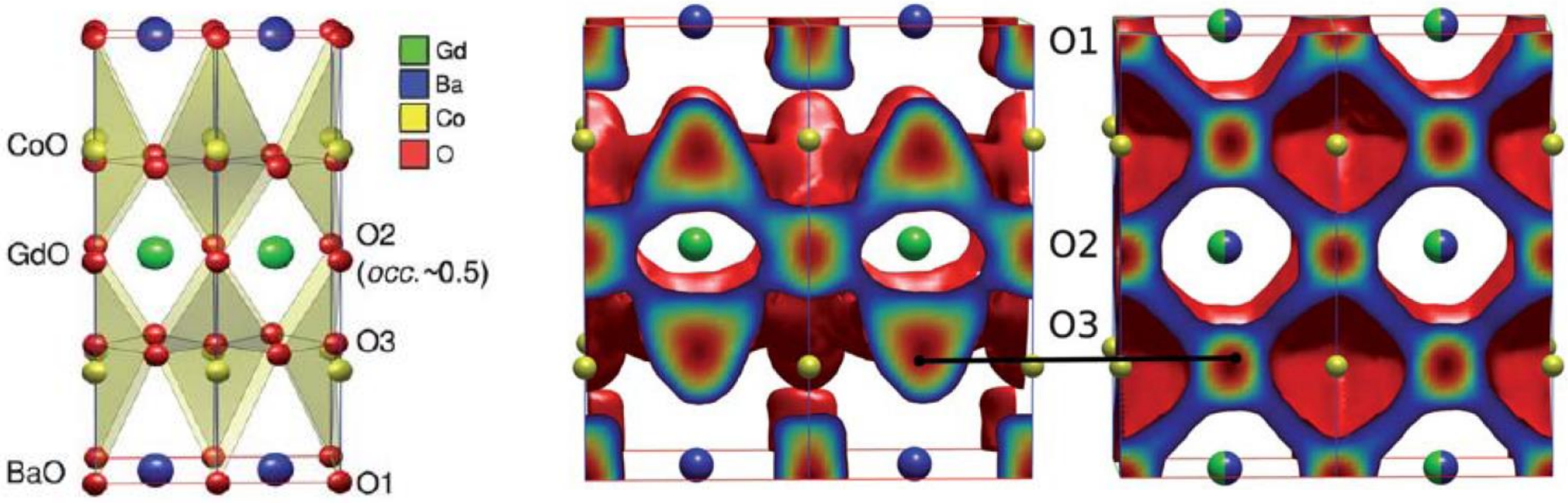




- Initially D rises quickly but then levels off.
- Increased FE of O_i due to the presence of other pre-existing O_i.
- Stiffening of the lattice by the extra O_i that pin the NiO_6 sublattice.
- E_m varies between 0.49-0.64 eV depending on δ.

Chroneos *et al.* Phys. Chem. Chem. Phys. **12**, 6834 (2010).

Modelling of SOFC & SOEC



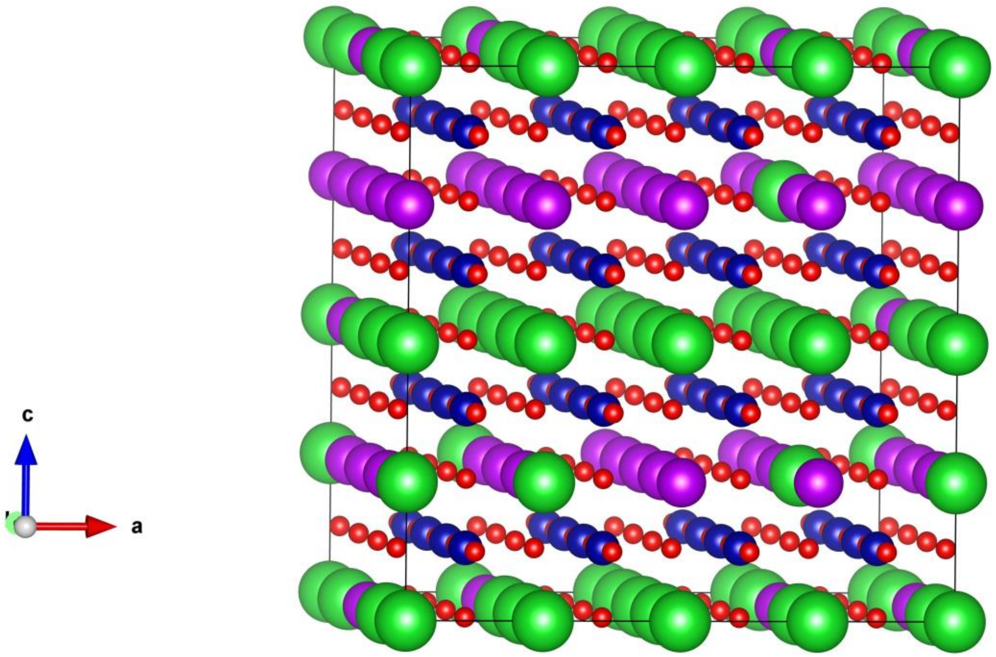
- ➢ Ordered: anisotropic diffusion (ab-plane).
- ➢ Antisite disorder: isotropic diffusion but with disorder diffusivities fall.

Design Criteria:

- ➢ Need ordered structure to optimise diffusivities.
- ➢ Need to grow crystal along ab-plane.

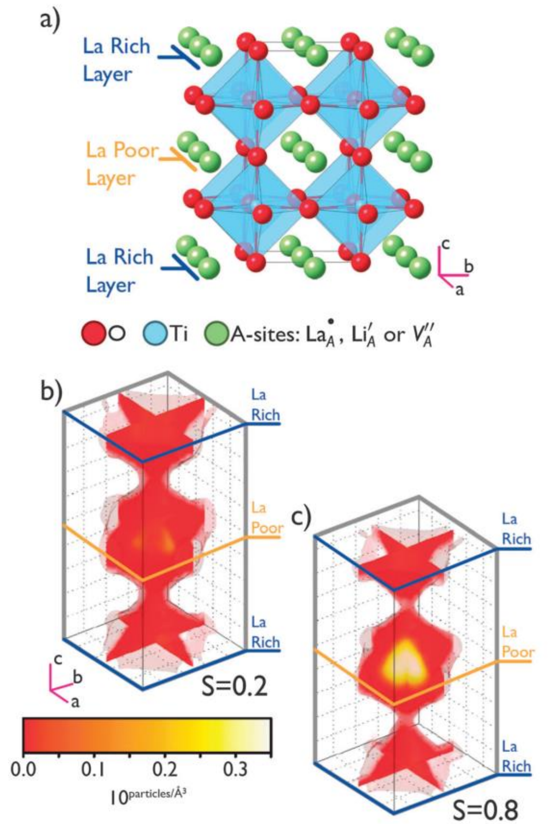
Chroneos *et al.* J. Mater. Chem. **21**, 2183 (2011).

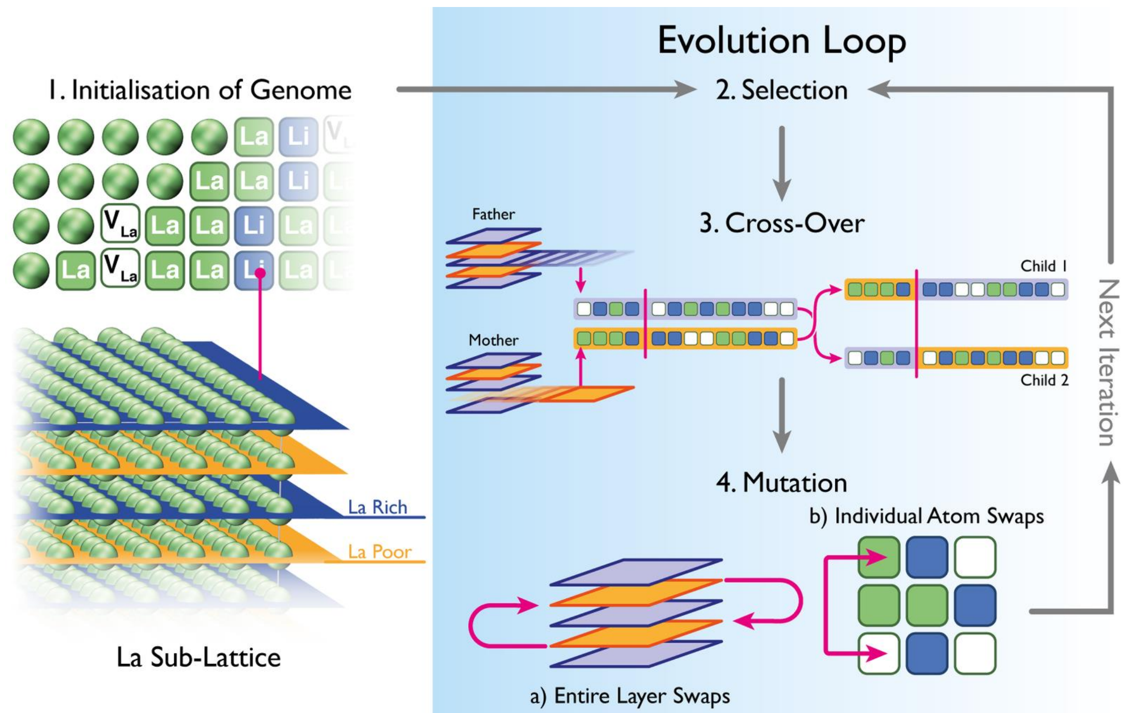
Future Perspectives: Use SQS + DFT



- **Work in progress:** Use the special quasirandom structures method + DFT to study antisite disorder and diffusion in double perovskites.
- This is an efficient way to describe the random nature of the local atomic environment and the distribution of antisites.
- 320-atomic SQS structures for the $(Ba_{1-f}Gd_f)_1(Gd_{1-f}Ba_f)_1Co_2O_6$ alloy. Green, purple, blue, and red spheres represent Ba, Gd, Co, and O atoms, respectively.

Genetics of Superionic Conductivity



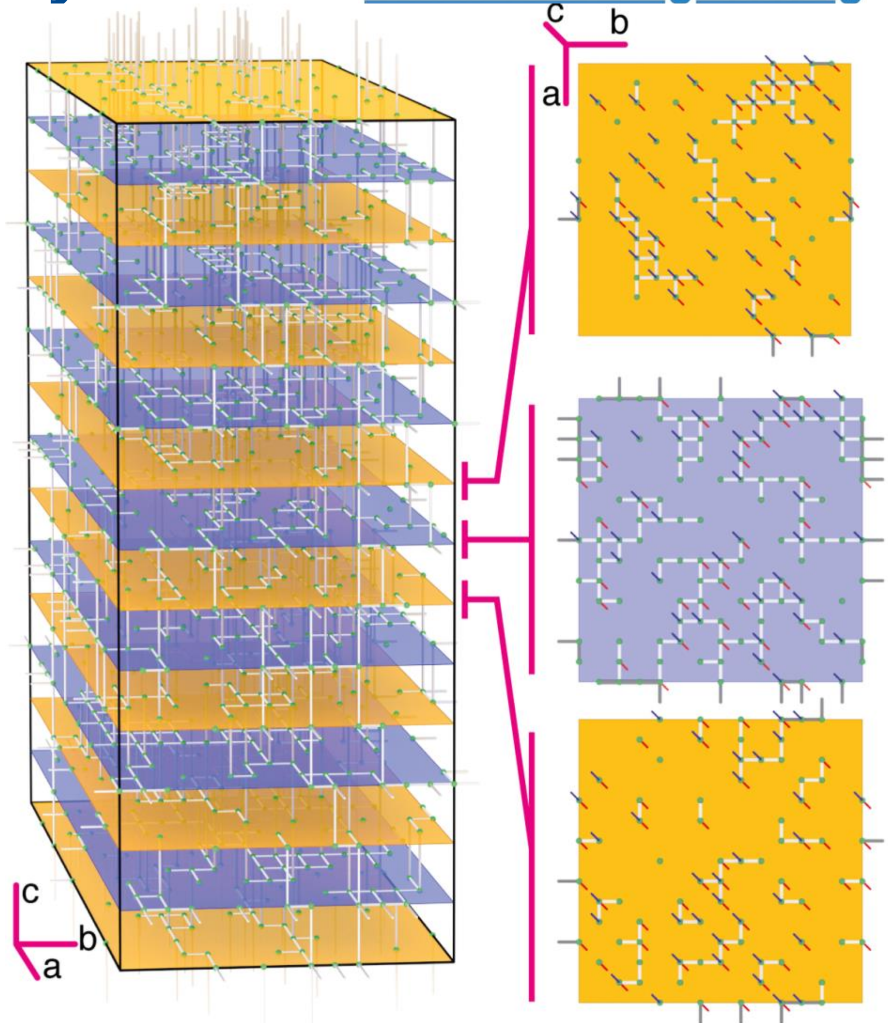


- Things can get very complicated structure-wise. Solutions? Mixed techniques MD & genetic algorithms.

Jay, Rushton, Chroneos *et al.* Phys. Chem. Chem. Phys. **17**, 178 (2015).

Genetics of Superionic Conductivity

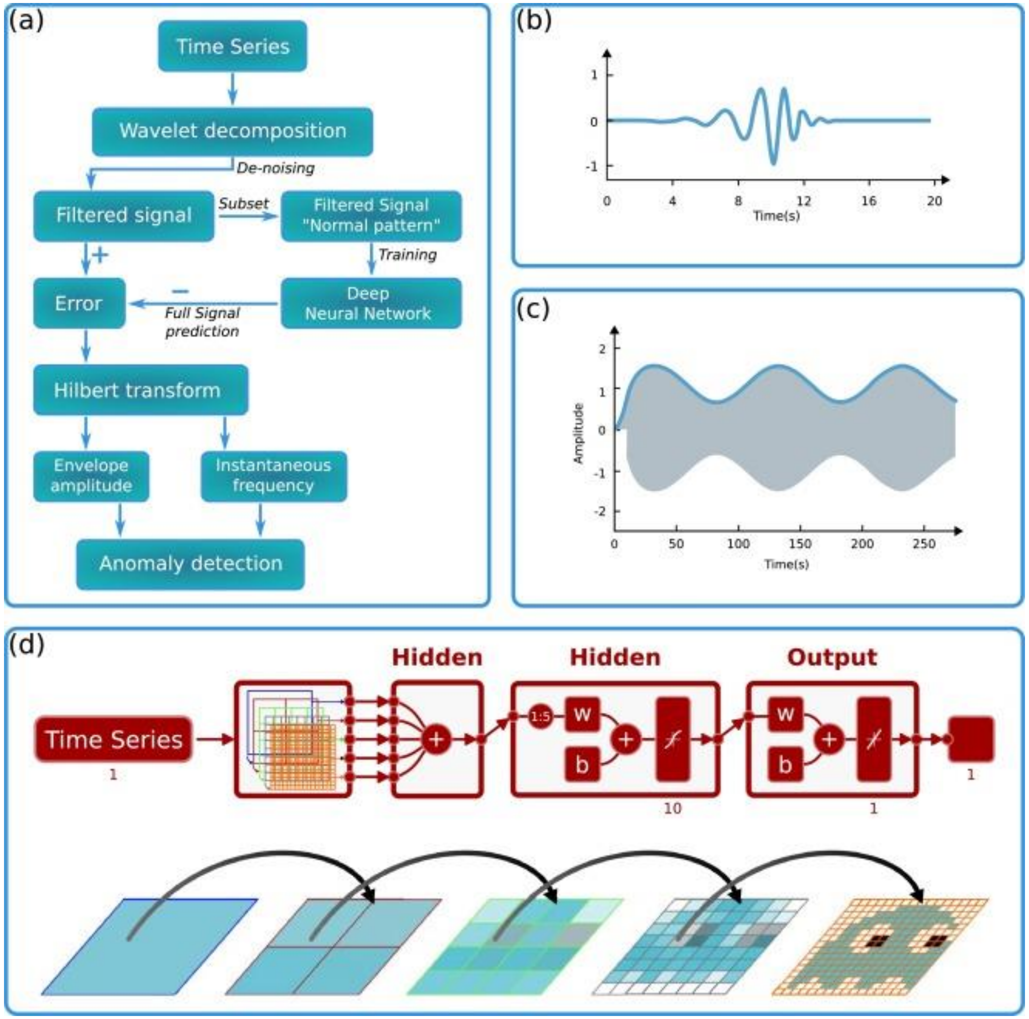
- We provide evidence that there is a 3D percolated network of Li diffusion pathways.
- We reproduces experimental ionic conductivity results.
- The method aids the investigation and optimisation of the properties related to superionic conductivity.
- Transferable method that can be used to provide insights into related materials with structural disorder for batteries, SOFC & electronics.



Jay, Rushton, Chroneos *et al.* Phys. Chem. Chem. Phys. **17**, 178 (2015).

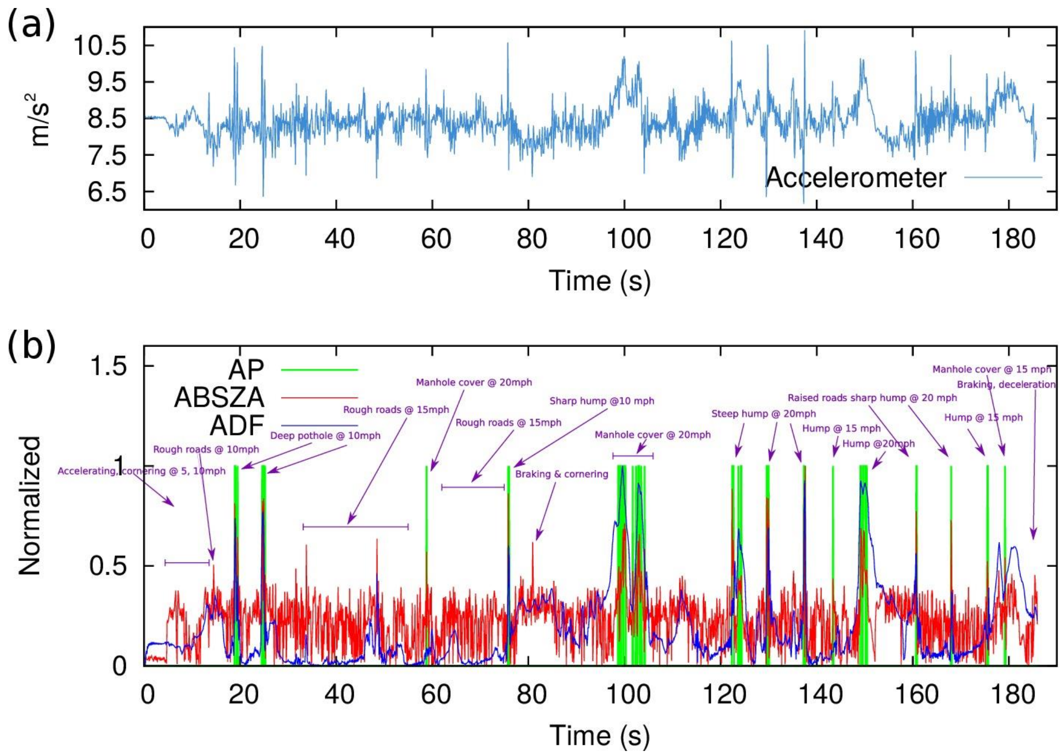
Future Perspectives: Anomaly Detection

- The algorithm combines wavelet analysis, nonlinear autoregressive neural networks and Hilbert transform.
- The wavelet decomposition filters out the noise embedded in the signal.
- The nonlinear autoregressive neural network is trained (normal operating conditions) to predict the output of the filtered signal.
- The error, measured as the difference between the neural network output and the filtered signal, is then analyzed using the Hilbert transform.
- If the amplitude and/or instantaneous frequency change significantly the pattern is anomalous.



Future Perspectives: Anomaly Detection

- **Method works** for Seismic electric signals (SES) emitted by rocks under stresses caused by plate-tectonic forces. SES are precursors for earthquakes.
- **Method does work** for road anomaly detection.
- **Work in progress**: Will it work for diffusion? Detecting anomalies in MSD prior to an atomic jump?



Kanarachos, Chroneos *et al.* Expert Systems with Applications in press

Summary

- ➢ Applied modelling: the simulations are used to interpret, guide and support experimental studies. Perform experiments wherever possible.

- ➢ Technologically important systems with a focus on energy applications (fuel cell, solar cell & nuclear materials).

Key collaborations over the past 10 years:

1. Imperial College London, Prof. Robin W. Grimes, Prof. John A. Kilner.
2. MIT, Prof. Bilge Yildiz.
3. Cambridge University, Dr Paul Bristowe.
4. Los Alamos National Laboratory, Dr Mike Cooper
5. University of Münster, Prof. Dr Hartmut Bracht.
6. Kharkov State University, Prof. Ruslan V. Vovk.
7. KAUST/Imperial College London, Prof. Udo Schwingenschlögl.
8. Purdue University, Dr Miltos Alamaniotis, Prof. Lefteri Tsoukalas
9. TEI Crete Prof. Vasilis Saltas, Prof. Filippos Vallianatos
10. University of Athens, Prof. Charalampos Londos

Funding: Rolls Royce (DP), Jaguar Land Rover (SK), Lloyd's RF (AC).

Coventry University

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CENTRE FOR Manufacturing & Materials Engineering

Thank you for your attention!