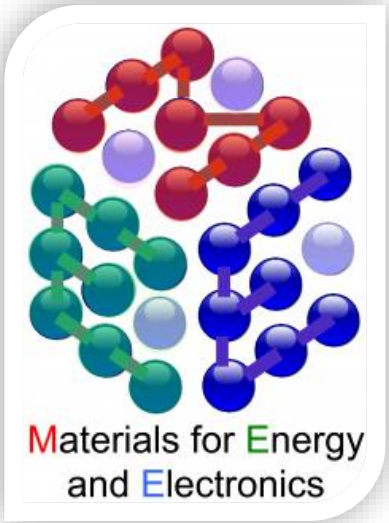
School of Physical Sciences

University of Kent

2020-2021

Materials Chemistry

Project Descriptions



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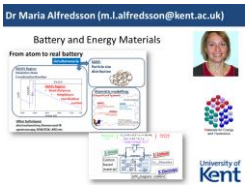
Computational and Experimental Studies of Environmentally Relevant Materials

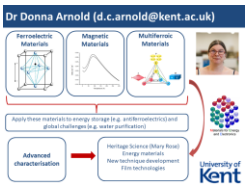


Supervisor: Dr Maria Alfredsson (m.l.alfredsson@kent.ac.uk)

The projects offered in our group deals with energy and environmental issues. We are currently working on systems associated with energy storage (batteries), solid oxide fuels cells, photo-voltaic materials (solar cells), sensors and soil remediation. We use a combination of experimental and computational techniques.

1. **Predicting XAS spectra for sulphate systems:** In collaboration with the University of Uppsala we have collected XAS data for the S K-edge in sulphate systems used as novel cathode materials in Li-ion batteries. The spectra show some interesting features, varying if we are working with transition metal ions (e.g. Fe) or alkaline earth ions (e.g. Mg). The aim of this project is to use quantum mechanical calculations to simulate XAS spectra and compare with experimental data to aid in the interpretation of the measurements. You do not need any previous knowledge about atomistic simulations. We also work on Li-sulphur batteries.
2. **Novel anode and cathode materials for Li-ion and Na-ion batteries:** Despite their wide spread applications, Li-ion batteries are still suffering from low energy capacity if they should be competitive in electrical vehicles. We need to find cathodes with higher voltage or anodes that can store a larger amount of Li/Na-ions. In this project you will synthesise and characterise novel cathode and anode materials for energy storage systems. If successful, they will be cycled as batteries. If you prefer we can use computer modelling to predict novel cathode and anode materials.
3. **Gas sensors:** A growing concern regarding burning of fossil fuels is the emission of CO_2 and NO_x originating, from, for example, diesel engines. In this project you will synthesise and characterise novel materials for CO_2 sensing. Part of the project will be to find a method of manufacturing these materials and test their sensing properties. The manufacturing could involve 3D printing of the sensors.
4. **Soil remediation using natural zeolites:** In a recent project it was found that natural zeolites are successful in remediating Pb from contaminated soils. Of particular interest was the fact that one of the zeolites seems to be pH independent, which is important when dealing with acid mine drainage. In this project you would synthesise and characterise a natural zeolite and by using analytical techniques, such as atomic absorption spectroscopy, investigate the cation exchange capacity of the zeolite

Multifunctional Metal Oxide Materials



Supervisor: Dr Donna Arnold (d.c.arnold@kent.ac.uk)

Dr Arnold's research interests lie in the area of multifunctional oxide materials. Both ferroelectric and magnetic materials form the cornerstone of many commercial industries including applications in healthcare instrumentation and diagnostic tools, electronics and energy storage, and sensors. Current industries dependent on magnetic and ferroelectric materials are faced by a number of important challenges, 1) in ferroelectrics the current material of choice in most applications is lead zirconate titanate (PZT); now widely considered to be unsafe due to the toxic nature of Pb, 2) how do we optimise magnetic materials for future applications and 3) how do we move towards next generation applications? Lead free multifunctional materials, which couple more than one property together such as multiferroics exhibiting magnetic and ferroelectric character, have the potential to deliver the next generation of devices moving us away from our PZT dependency. For example multiferroic materials are expected to provide next generation of memory which can be electrically written and magnetically read (or vice versa) providing lower power faster alternatives to current technologies.

Typical research conducted within Dr Arnold's group involves the synthesis of novel metal oxides materials by conventional solid-state techniques. These materials will then be characterised using x-ray diffraction, Raman, SEM and their functional properties characterised using techniques such as SQUID magnetometry, electrical characterisation.

Potential projects include:

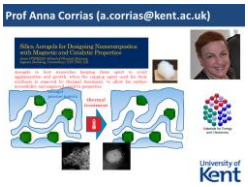
Multiferroic materials: This project looks at exploring perovskite materials to incorporate both ferroelectric and magnetic behaviour into a single material. In addition to traditional multiferroic materials we are also interested in ferrotoroidal materials in which the Physics and Chemistry offer exciting opportunities for multifunctionality.

Exploring Rutile materials for multifunctionality: We have a new project which is looking at exploring the flexibility of trirutiles to provide new materials with increased functionality.

Antiferroelectric materials for energy storage: We are interested in the synthesis of new antiferroelectric materials which provide a new technology for large scale energy storage.

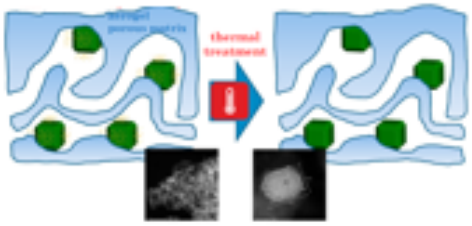
Geometrically frustrated materials: In geometrically frustrated materials the magnetism is incompatible with the underlying crystal structure. This often leads to exciting magnetic phenomena and we are interested in how we can control frustration in materials.

Synthesis and characterization of nanomaterials and poorly crystalline solids

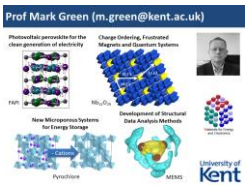


Supervisor: Professor Anna Corrias (a.corrias@kent.ac.uk)

The project(s) will deal with the synthesis and/or characterization of novel nanomaterials and poorly crystalline solids, with the ultimate aim of studying the structure/properties relationship. Nanomaterials exhibit many interesting chemical, physical and mechanical properties and they can be used in a large range of applications spanning very different fields. To name a few nanoparticles can be used as contrast agents in Magnetic Resonance Imaging, as very effective catalyst and as next generation computer chips. Their peculiar properties stem from the large fraction of atoms in the material which are located in the surface, i.e in not fully coordinated sites. For this reason the synthetic methods to produce nanomaterials are focussed in achieving control on the size of the nanoparticles which ultimately dictate their final properties. This can be achieved, for example, dispersing them in highly porous supports, such as aerogels, that can hinder coalescence and growth and at the same time provide additional peculiar properties. The detailed characterization of these materials is carried out using a multitechnique approach that may include X-ray diffraction, nitrogen physisorption at 77K, electron microscopy, thermal analysis and X-ray absorption spectroscopy.



Functional Materials by Design



Supervisor: Professor Mark Green (m.green@kent.ac.uk)

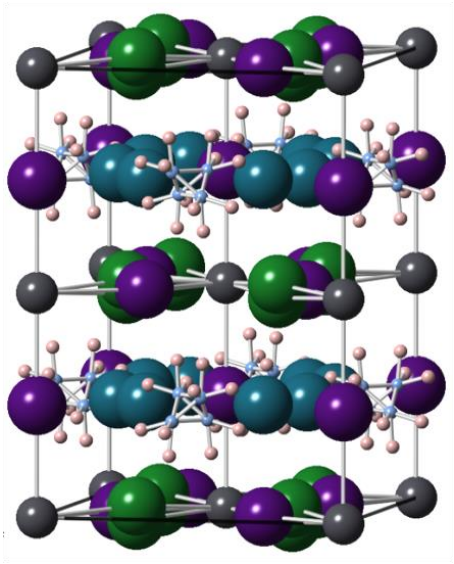
The synthesis and characterization of new functional materials is essential for progress in a vast array of crucial applications for human safety, security and prosperity. Our research program focusses on new materials that have specific relevance to the electronics and energy industries. For example, new solar, battery and magnetic materials that offer alternative electrical energy production and storage solutions to replace the current reliance on toxic gas emitting fossil fuels.

The work involves in-house synthesis and characterization with a state-of-the-art suite of instrumentation. In particular, we develop and implement new techniques and procedures for the chemical manipulation of solid-state materials, which provide new strategies to generate functional materials by design. We extensively use national facilities in Europe and worldwide such as neutron sources at NIST (USA), RAL (UK) and the ILL (France) and in synchrotron sources in ESRF, France and Diamond, UK. We have ongoing collaborations and joint students with the University of Lille, particularly in solid state NMR measurements.

The following are four representative projects and publications:

Photovoltaic perovskite for the clean generation of electricity

Global warming is now dangerously high; some claim that the International Panel on Climate Control's target of 1.5% this century could be exceeded by 2040 causing massive global issues. The sun generates enough energy to provide the world with all its power demands many times over. For example, an average house could operate on 10% of the sunlight energy that illuminates it and be entirely carbon free. Current solar energy technology has poor energy conversion and is prohibitively expensive. We are developing new perovskite photovoltaics materials that offer unoresendented improvements in both cost and performance. We are particularly focused on developing coatings that can be incorporated in existing structures, creating new alternative energy opportunities.



Structure of perovskite photovoltaic that offer the next generation of high performance solar technology.

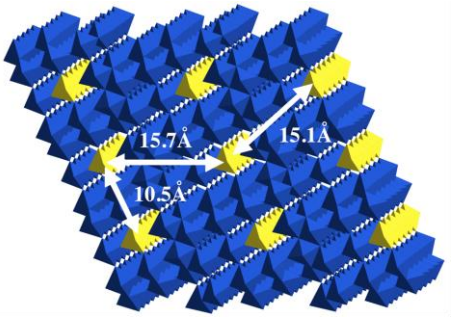
Minns, J. L *et al*., *Structure and interstitial iodide migration in hybrid perovskite methylammonium lead iodide* Nat. Commun. 2017, 8, 15152

Songvilay, M *et al*., *Common acoustic phonon lifetimes in inorganic and hybrid lead halide perovskites* Phys. Rev. Mater. 2019, 3, 093602

Charge Ordering, Frustrated Magnets and Quantum Systems

Charge ordering is becoming an increasingly important issue in understanding the electronic structure of complex transition metal oxides. It finds applications in advanced materials such as superconductors, magnetic storage devices, multiferroics and quantum computing. This project explores series of mixed d^0/d^1 compounds that are susceptible to charge ordering, to (i) develop predictive rules and understand the decisive factors controlling the ordering of valence states and (ii) tailor new electronic ground states to produce novel low

dimensional localised and delocalised structures, with particular emphasis on those that are analogous to molecular systems.



Structure of $Nb_{12}O_{29}$ forming ordered chains of Nb^{4+} that undergo a transition to a magnetically long ranged ordered state.

Kruk, I. *et al*., *Titanium doping of the metallic one-dimensional antiferromagnet, $Nb_{12}O_{29}$* Inorganics 2019, 7, 66
Zajdel, P. *et al*., *Structure and magnetism in the bond-frustrated spinel $ZnCr_2Se_4$* Phys. Rev. B 2017, 95, 134401

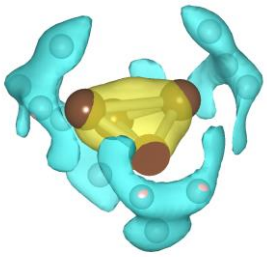
New Microporous Systems for Energy Storage

A wide variety of Li-ion batteries are currently commercially available for many applications. These batteries are extremely expensive to manufacture, have major cycle fading issues due to the layered nature of the structure, and have to be disposed of in specific ways. There has been a major research effort recently to identify new batteries based on Na or other metals to reduce costs and cycle fading. These batteries would be much more useful in a diverse range of applications, such as part of an off-grid solar-battery power hub providing vital energy in remote areas.

Kruk, I. *et al*., *Coupled commensurate cation and charge modulation in the tunneled structure $Na_{0.40(2)}MnO_2$*. J. Am. Chem. Soc. 2011, 133, 13950

Development of Structural Data Analysis Methods

Conventional powder or single crystal structural analysis of constant wavelength X-ray or neutron diffraction data, provides information on the content of a unit cell in the form of the location of a group of atoms and their corresponding thermal parameters. For most applications, this provides sufficient information. However, for certain materials particular those relevant to energy applications, such as oxide ion conductors, batteries, charge ordered systems or gas absorbing porous materials, components of their structure are not well described within this model and it does not fully provide the complete picture of the nuclear and electron densities. This project uses computational methods to gain deeper understanding of the structure from data largely obtained at national facilities such as neutron and synchrotron facilities.

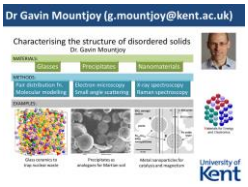


Nuclear scattering density map of CH_3NH_3 molecule as derived from the Maximum Entropy Method showing C and N (yellow) and hydrogen scattering (blue)

Kuang, X. *et al*., *Interstitial oxide ion conductivity in the layered tetrahedral network melilite structure* Nat. Mater. 2008, 7, 498
Nakatsuji, S. *et al*., *Spinorbital short-range order on a honeycomb-based lattice* Science 2012, 336, 559

These are representative projects, but we work on a number of other energy and electronic materials projects including molecular magnets, metal – organic frameworks, iron based superconductors and inorganic – organic hydrids.

New glass structures for communication, energy and medical applications



Supervisor: Dr Gavin Mountjoy (g.mountjoy@kent.ac.uk)

I am very interested in non-crystalline solids, i.e. glasses. The atomic structure determines the properties and hence applications of new glasses. Applications studied in my recent projects include: fibre optic communication, orthodontics, and battery materials. The methods used include lab-based structural characterisation (e.g. Raman spectroscopy), analysis of data from synchrotron laboratories (e.g. x-ray absorption spectroscopy), and molecular modelling. The structural features which have been studied in recent projects include lanthanide ion sites in relation to luminescence, network connectivity in relation to durability, and alkali ion diffusion in relation to conductivity.

webpage: https://www.kent.ac.uk/physical-sciences/people/363/mountjoy-gavin

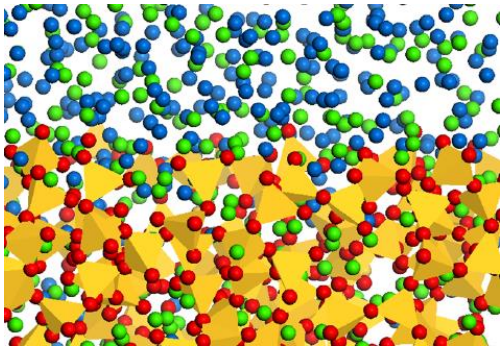
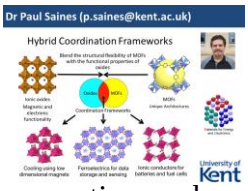


Figure: atomic structure of chlorine containing calcium silicate glass for orthodontic applications.

Coordination frameworks with magnetic and electronic properties



Supervisor: Dr Paul Saines (p.saines@kent.ac.uk)

Many modern technologies rely on materials with useful magnetic and electronic properties, such as ferromagnetism and ferroelectricity. While such behaviour is commonly associated with metal oxides recently a new class of compounds, coordination frameworks, have emerged with such properties.[1] These compounds have inorganic cations bridged by organic ligands, leading to the adoption of unique extended architectures, with exceptional flexibility in composition and properties. They show promise as ferroelectrics with responses over broad temperature ranges, useful for precision mechanical motors,[2] and multiferroric materials, whose magnetic properties can be modified by an electric field, potentially useful for data storage.[3] They often adopt highly anisotropic structures with isolated magnetic chains and sheets, allowing us to probe the exotic magnetism in these low dimensional structures, which can potentially be used for magnetic cooling.[4] Most recently they have also demonstrating the ability to conduct protons and Li cations, which could be potentially used for generating energy in cleaner and more efficient ways.

Our group has interests across all of these areas and projects are available in any of these to match a student's interests. In many cases the properties of coordination frameworks emerge from origins unique to these materials. There is a critical need to understand how their complex atomic-level structures give rise to these important physical properties. Projects will typically focus on making and characterizing new coordination frameworks, using a combination of in-house single crystal and powder X-ray diffraction and magnetic and electronic property measurements. The balance of synthesis and characterization depends on the project and the student.

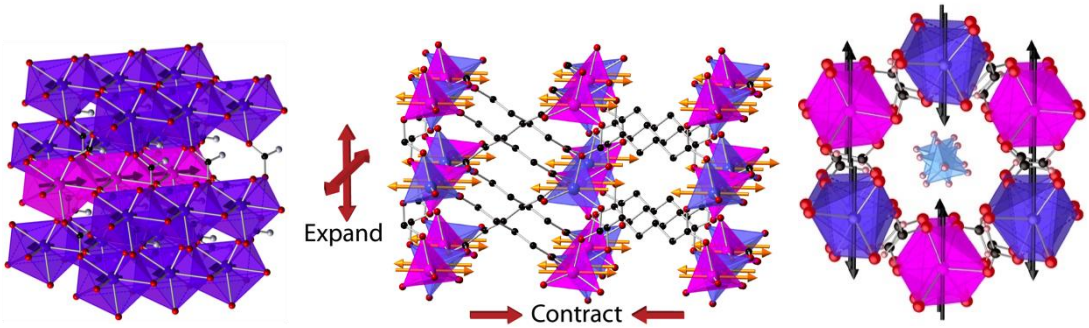
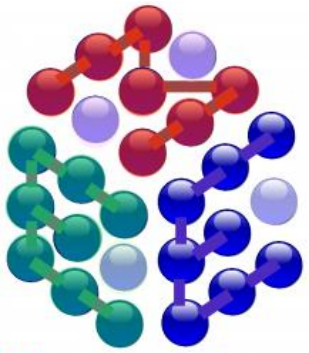


Figure: Structure of left) Magnetocaloric $Tb(HCO_2)_3$ featuring 1D ferromagnetic chains packed in an antiferromagnetic triangular lattice, middle) Co(adipate) which shrinks in one dimension as it magnetically orders due to its anisotropic magnetic coupling and right) multiferroic $NH_4Co(HCO_2)_3$, which has ferroelectric properties across a broad temperature range.

1. A. K. Cheetham *et al*., *Science*, 2007, **318**, 58; C. N. R. Rao *et al.*, *J. Phys.: Condens. Matter*, 2008, **20**, 083202.
2. J. M. M. Lawler *et al*., *Dalton Trans.*, 2015, **44**, 11613.
3. L. C. Gómez-Aguirre *et al*., *J. Am. Chem. Soc.*, 2016, **138**, 1122.
4. P. J. Saines *et al*., *Mater. Horiz.*, 2015, **2**, 528.



A broad range of expertise in developing materials key for energy and electronics applications. This includes creation of new materials, physical property investigation and developing the understanding of their atomic, magnetic and electronic structures, crucial to optimising their properties.

Contact details MEE-group: Dr Paul Saines *; **email : P.Saines@kent.ac.uk***