NEW ULTRAHARD MATERIALS FOCUS AREA

Objective: Efficient simulation of capacitor electrode materials

After the PhD student involved in these studies had left the CoE-SM, a replacement could not be found, and attempts to recruit a candidate for a postdoc position were unsuccessful. Therefore, the research activities in this area are currently stalled. In 2020, Prof. A. Quandt co-authored an experimental study of molybdenum disulfide powder as a potential new electrode material for supercapacitors. (A. Quandt, R. Warmbier and G. Seifert)

Objective: Solar cell device simulations

More focus has been given to fundamental light-matter interactions in a solar cell, and an article summarising the Group's findings, which also features the concept or rate equations and their various applications, was published. New material for a review article in *Optical Materials Express* was prepared, after being invited by the Editors to present a paper about solar cell simulations using *ab initio* methods. Furthermore, a new MSc student (M. Zdravkovich) was recruited to take over some of these simulations in 2021, and hopefully beyond. (A. Quandt and R. Warmbier)

Objective: Ab initio and multi-scale simulations of strong materials

The computer cluster is currently running 14 machines totalling about 5.4 TFlops computer power and 1552 GiB of RAM. In 2020, one machine was added to the cluster. As in previous years, The FAC continued to support a large variety of computational tools for materials simulations, and work on efficient numerical interlinking of these codes. Prof. Quandt has published a conceptional paper about a new approach to the many-electron problem, which offers an alternative approach to density functional theory, which is marked by a similar numerical effort, but potentially has much higher accuracy. It is hoped that these ideas will be implemented in existing programme packages in coming years. Dr Warmbier wrote a new program to calculate Raman intensities of materials for the GPAW *ab initio* code. This allows the inclusion of up to 400 atoms per unit cell, a factor of 10 more than previously possible with the old Quantum Espresso implementation. (R. Warmbier and A. Quandt)

Objective: Water desalination using nano-porous GO membranes

A paper has been published in 2020, which exposed the suggested "superflow" of water through nano-porous graphite oxide (GO) membranes as nothing more than just hot air. Beyond that, the paper also contains a detailed study of a large variety of membrane models, which should be useful to model practical scenarios of fluid flow through porous membrane materials. (A. Quandt, G. Seifert and D. Tomanek)

Objective: Topological materials

The Group started the development of a program package to implement and characterise different topological model Hamiltonians, including computation of invariants and explicit real-space computation of surface states. A resulting paper for the full characterisation of the 2D SSH model is in preparation. The possibilities of using *ab initio* band structures of real materials to obtain realistic model parameters have been investigated, but more work is needed. The Group has also studied the occurrence of topological effects in special waveguide arrays etched into glasses, and published some of the findings. Another interesting aspect of the studies of waveguide arrays was the occurrence of rogue waves in nonlinear waveguides, which was published in a paper. Prof. Quandt has also published a paper about winding numbers and fundamental algebraic aspects of topological materials, which is currently in press. These studies will be real topological materials based on ceramics and other strong materials, together with detailed studies of perturbation theory for topological band structures, and the use of Green's functions to achieve a proper many-body description of topological materials. (A. Quandt, R. Warmbier, C. Pelwan and C. van Niekerk)

Objective: Strengthening of CNTs through sp^3 bond creation

As an independent extension of a related project with Prof. Hearne, the Group studied the creation of sp^3 bonds on defect decorated single wall CNTs using pressure and shear strains using Molecular Dynamics simulations. As a secondary research goal, the Raman signature of different defect structures was investigated. Results will be presented in Mr. Maphisa's MSc dissertation mid-2021 and resulting publications. (R. Warmbier and X. Maphisa)

Objective: Synthesis and characterization of luminescent nanomaterials for solar cells, solid state lighting and gas sensing applications

The Group did not make a good progress in 2020 due to limited access to the laboratory during the nationwide COVID-19 lockdown. However, a few students did some work. For example, Ms Prettier Maleka (PhD) whose project is on the preparation and characterization of inorganic caesium lead iodide perovskite ($CsPbI_3$) for photovoltaic applications. She made considerable progress on the theoretical calculations of lattice parameters and formation energies for $CsPbI_3$ using density functional theory (DFT). She has prepared a draft manuscript to report phase stability, electronic structure and optical properties of $CsPbI_3$. She could not visit University College London-UCL as planned for fabrication and testing $CsPbI_3$ photovoltaic cells due to traveling restrictions, an online meeting was held with the UCL collaborator.

Mr Fekadu Ayele (PhD), whose project is on the $CuInS_2$/ZnS/ZnS core-shell quantum dots, also could not visit the Korea Institute of Science and Technology (KIST) to fabricate and test quantum dots light emitting diodes. Instead, the were sent samples to KIST for preliminary testing, but they did not yield good results. He has prepared two draft manuscripts. The project has been modified slightly to enable him to complete his study before the end of this year.

Ms Charsline Gatsi (PhD) made considerable progress on the synthesis and characterisation of Ga_2O_3 nanostructures. She is planning to spend some time at the CSIR to use the gas sensing facility to evaluate the gas sensing properties of her Ga_2O_3 nanostructures.

Mr Teboho Matsoha (MSc) completed all the experiments on the synthesis, characterisation and performance testing of Ga/Mg-ZnO nanomaterials on organic photovoltaic cells. He is planning to submit his dissertation for examination by the end of March 2021.

Thabang Melato (PhD) needs to start synthesising bulk heterojunction P3HT:2,3,4-OMe-PCBM and PTB7-Th:2,3,4-OMe-PCBM OSCs photo-active layers. In 2020, he only managed to be trained on UJ's newly installed and commissioned state-of-the-art quanta master 800 spectrofluorometer.

Overall, most of the objectives set for 2020 could not be achieved, and everyone hopes to do better in 2021. (Ms P. Maleka, F. Ayele, Ms C. Gatsi, T. Matsoha, T. Melato and M. Ntwaeaborwa)

Objective: Irreversible nanotube interlinking using combined ion-implantation pre-processing, high pressures and high temperatures

Low-fluence light-ion ($^{11}B^+$) high-energy (150 keV/ion) implantation pre-processing of double walled carbon nanotubes (DWCNTs) has been effected to 'decorate' them with defects. These are intended to serve as nucleation sites for potential sp^3 interlinking between tube walls in proximity upon strong deformation of the tube cross-sections under cold compression to 20-25 GPa in diamond anvil cells. The pressure response of such implanted DWCNTs is monitored *in situ* using Raman spectroscopy, and compared with those of pristine reference DWCNTs. Pressure dependences of the G mode frequency and D to G band intensity-ratio, and radial breathing modes have been monitored. The light-ion low-fluence implantation lowers the threshold pressure for deformation of tube cross-sections to high-curvature profiles decorated with defects, rendering suitable tube local environments for interlinking. The question whether irreversible sp^3 interlinking at low volume fractions is

discerned in the Raman data from implanted tube bundles under compression, and the stability of such bonding have been considered. Simulations by Dr Warmbier using semi-empirical REAX force fields suggest that vacancy-assisted interlinking in DWCNTs forms stable sp^3 bonds both within a DWCNT and across CNTs. This work has been submitted to *Phys. Rev. Materials* and the reservations and recommendations of the reviewers are being resolved.

It is planned to extend beyond the above-mentioned first phase of cold compression studies, to implement a multi-stimuli approach including low-fluence C-ion or He-ion implantation pre-processing at different fluences, high-pressures and CO_2 laser heating of both DWCNTs and single-walled CNTs (SWCNTs). The rationale for this implantation strategy is to limit defect production to that of single vacancy (point) defects. The Raman spectroscopy signatures described above are key to probing for wall-to-wall (outer-to-inner and outer-to-outer) interlinking. Collaborators are Prof. Mervin Naidoo (for the implantation work) and Dr Rudolph Erasmus for the Raman investigations (VIS-Raman and UV-Raman). Further plans include the numerical characterisation of the Raman signature of different defects and interlinks in CNTs to assist with the interpretation of experimental data. Molecular dynamics simulations combining different defect, pressure and temperature regimes are planned to give further inside into defect proliferation and sp^3 creation processes. Mr Liberty Kapesi, who completed his MSc with distinction during 2018, registered for a PhD in 2019 to implement these multi-stimuli experiments, and his work is ongoing. (G.R. Hearne, L. Kapesi and R. Warmbier)

Objective: Pressure-induced spin crossover in nanoporous host-guest framework structures

The aim of the study is to investigate pressure effects on spin crossover (SCO) behaviour in porous crystalline structures, in particular metal organic framework (MOF) compounds. These MOFs involve ferrous iron (Fe(II)) centres with coordinated organic ligands, which form linkers between neighbouring Fe(II) metal centres. SCO involves the spin-pairing of 3*d* electrons in low-lying orbitals with attendant changes to magnetic behaviour and bond lengths. The MOFs act as a host when guest molecules penetrate the framework and occupy void space within. At a specific temperature, the guest molecules interact with the metal centres of the MOF and trigger SCO. By the application of pressure, more guests are forced into the MOF, thus increasing the guest density within the framework. Guest-to-ligand interactions trigger high-spin (paramagnetic) to low-spin (diamagnetic) switching in most metal-ion cores, thus rendering potential pressure sensor or actuator capabilities. Pressurisation should tune the SCO transition temperature to higher temperatures as the amount of metal centres which interact with the guests increases, and smaller unit-cell volumes are attained where the low-spin state is energetically (enthalpically) favoured. This phenomenon is investigated for varying bipyridyl derivatives constituting the linkers of the framework and guests incorporated into void space. The aim is to attain high SCO temperatures, near room temperature, with a major fraction of the Fe atoms undergoing SCO. In this regard, first successful experiments have been completed on the $[(Fe_2(azpy)_4(NCS)_4)\bullet(G)]_n$ MOF, where G = guest molecule. This has been published in ChemPlusChem (see doi.org/10.1002/cplu.202000557), as part of the MSc research of Mr R. Goliath. First attempts at a Raman characterisation of the MOF at ambient conditions were made successfully, and interpretation of the Raman spectra have been aided by the calculations of Dr Warmbier. Raman pressure studies are planned for the near future to investigate the structural changes at SCO. (G.R. Hearne, B. Vatsha, R. Goliath and R. Warmbier)

Objective: Optical characterisation of rare-earth doped ZnO

Site-selective laser spectroscopy of rare-earth doped ZnO is ongoing. The need for monovalent charge compensation has been established and demonstrated by the significant increase in emission in powders co-doped with Li^+. In films, the emission remains quite weak,

possibly due to remote and sparse charge compensating impurities. It is not immediately obvious how intentional charge compensation can be achieved in the films. Outputs of N.C. Gatsi's MSc project (2019 graduation) were realised in 2020. The work on ZnO:Nd^{3+}:Li^{+} has been published, while that for ZnO:Nd^{3+} films has been submitted for consideration. The effects of double doping with other rare earths are being investigated in the powder samples. Collaboration continues with Dr R.A. Jackson of Keele University, UK and Prof D Wamwangi. (M. Mujaji)

Objective: Radiation Damage Assessment of materials used in the TILECAL section of the ATLAS detector at the Large Hadron Collider at CERN

The radiation damage to the optical properties of plastic scintillators is being assessed following irradiation using a 6 MeV proton beam produced by the 6 MV tandem accelerator of iThemba LABS, Gauteng. A comparative is drawn between polyvinyl toluene based commercial scintillators EJ200, EJ208, EJ260 and BC408 as well as polystyrene based scintillator UPS923A and scintillators manufactured for the TILECAL. Results on the proton induced damage so far indicate a reduction in the light output and transmission capability of the plastics. Scintillators containing a larger Stokes shift, i.e. EJ260 and EJ208 exhibit the most radiation hardness. The EJ208 is recommended as a candidate to be considered for the replacement of Gap scintillators in the TILECAL for future upgrades. Research is also being conducted on new low electron work function materials which can be radiation hard in order to be used in neutron exposed photomultipliers. In addition, radiation hardness of different optical fibres in the TILACAL – ATLAS detector is being investigated. (E. Sideras-Haddad)

Objective: Magnetic ordering in diamond induced by proton irradiation

The investigations of the magnetic properties of ultra-pure type-IIa diamond following irradiation with proton beams of ≈1-2 MeV energy continue. SQUID magnetometry indicates the formation of Curie type paramagnetism according to the Curie law. Raman and photoluminescence spectroscopy measurements show that the primary structural features created by proton irradiation are the centers: GR1, ND1, TR12 and 3H. The Stopping and Range of Ions in Matter (SRIM) Monte Carlo simulations, together with SQUID observations, show a strong correlation between vacancy production, proton fluence and the paramagnetic factor. At an average surface vacancy spacing of ≈1-1.6 nm and bulk (peak) vacancy spacing of ≈0.3-0.5 nm Curie paramagnetism is induced by formation of ND1 centres with an effective magnetic moment μ_{eff}~(0.1-0.2) μB. (E. Sideras-Haddad, J. Mdhuli, M. Madhuku, T. Gkanetsos, M. Hernandez-Garcia, M. Ramos and A. Zuchiatti)

Objective: Investigation of novel synthesis methods of nanomaterials based on laser-solid interactions

New and novel approaches for the synthesis of Carbon Nanospheres (CNS) based on the interaction between UV laser irradiation and the surface of HOPG crystal and Carbon-like-diamonds were investigated. The required phase transition from an ordered crystalline form of carbon to a spherical nanostructured carbon was mediated by a laser induced shockwave during the impact of high-power laser pulses of a short wavelength on the HOPG flat surface. The direct laser irradiation of the surface of a HOPG crystal takes place in hydrogen atmosphere. The interaction of successive laser pulses with the HOPG surface results in a laser ablation process. The plausible mechanism responsible for the effect is related to the formation of a vapour cloud with compressed pressure and extreme high temperature which is known as the vapour plume. As the vapour plume plasma expands, recoil pressure creates different regimes of shockwaves of extreme shock pressure which propagates along the surface of the HOPG sample. The temperature and pressure carried by the shock wave, as it travels to different regions from the epicentre of the impact to the outer region, ultimately define the conditions for the required carbon phase transition and promotion of micro and nanostructure growth. The essential catalytic role of hydrogen during the first steps of CNS nucleation is being investigated. Critical parameters such as energy density, repetition rate, number of pulses, and the hydrogen content are being investigated in order to optimise the

synthesis conditions as well as to obtain a better insight into the complex physical processes and growth mechanism responsible for the formation of CNS. (E. Sideras-Haddad, O. Mouane, D. Wamwangi, G. Peters, T. Gkanetsos and A. Forbes)

Objective: Structure – Property relations in mixed metal oxide and related energy materials

This encompassing project studies the synthesis as well as structure-property relationships of selected series mixed metal oxide and related functional materials, mostly as electroceramic energy materials.

During 2020, investigations into solid oxide fuel cell electrolyte materials with improved oxide ionic conductivity at lower temperatures were continued. The main focus has been around bismuthate and cerate materials. The aim is to improve the stability and ionic conductivity of these materials by doping, co-doping and triple-doping. The effects of the type, concentration and ratio of dopants are studied in terms of the stabilised phase structure (mainly determined by X-ray diffraction and Raman spectroscopy) and how this is correlated to the ionic conductivity (as determined by impedance spectroscopy), all at variable temperature up to ~900°C. High resolution X-ray diffraction and pair distribution function measurements were also done on selected samples via mail in at NSLS-II at the Brookhaven National Laboratory in the USA. It is the intention to gain a better understanding of the overall functioning of these materials by looking at a comprehensive set of studies. So far, the complexity in these systems have been demonstrated and the limitations of the various techniques used for analysis highlighted. There is a clear need not only for the range of complementary techniques, but also for the variable temperature measurements to gain a full understanding of these systems, and to not unintentionally misinterpret data, which could so easily be the case when looking at results in isolation. There have also been investigations into the ageing of materials, either by degradation of phases or by ordering of oxide ions, both of which affect the long-term performance as an electrolyte. A post-doctoral fellow, four PhD, three MSc and two Honours students worked on this project in 2020. Many of the individual projects of senior post graduate students individually have also matured to the point, where draft publications are underway for submission in the near future. Most of the students are also expected to complete these projects during 2021.

A more long-term objective would be to combine the prepared materials into a proof-of-concept device. (D.G. Billing, C. Billing, D.W. Wamwangi, R. Erasmus, T.S.P. Mkwizu, M.J. Mnguni, M.A. Kiefer, S.M. Masina, M.S. Arshad, D. Malihase, M. Ramafemo and D. Fynn)

Objective: Cathode materials for the next generation of rechargeable lithium ion batteries

Fundamental structure-property studies of selected phosphate cathode materials are being done. The objectives of this study comprise the determination of the optimum synthesis conditions, as well as the underlying structure-property relationships of the materials. Significantly during 2020, various measurements were completed on the prepared materials, notably Mossbauer studies and preliminary synchrotron based studies, including EXAFS and XANES measurements, as well as the group's usual preferred range of techniques. Most of these materials are prepared via a range of steps, and the ultimate product obtained, along with its properties and composition, is generally critically dependent on the details of these steps. This is suggestive of rather complicated phase behaviour in these systems, and for which phase diagrams have not yet been published. Overall, the future intention is also to investigate the impact of doping and other chemical variations on the materials' properties, as well as assessing their suitability for use as cathode materials. (M. Thiebaut, G. Nkala, M. Nyoni (PT), E.E. Ferg (NMU), R.P. Forbes, C. Billing, D. Naidoo and D.G. Billing)