University Alliance
Doctoral Training Alliance

DTA3/COFUND Programme Research Project Proforma

Page 1 – General Information

Project Code	SHEN02
Partner University	Sheffield Hallam University
Faculty/School/Department/Research Centres	Science, Technology and Arts/Dep. of Maths & Engineering/MERI
First supervisor Please provide name and weblink	Dr Antonio Feteira https://www.shu.ac.uk/about-us/our-people/staff-profiles/antonio-feteira
Second supervisor Please provide name and weblink	Dr Tom Ostler https://www.shu.ac.uk/about-us/our-people/staff-profiles/thomas-ostler http://tomostler.co.uk/
Third supervisor Please provide name and weblink	Dr Iasmi Sterianou https://www.shu.ac.uk/about-us/our-people/staff-profiles/iasmi-sterianou
Fourth (external) supervisor	Dr D. Wang - University of Sheffield
External/industrial supervisor	Dr Tim Comyn, CTO Ionix Advanced Technologies Ltd
Which of the supervisors listed above is an early-career-researcher	Dr Tom Ostler
Contact details for project for informal applicant queries	Dr Antonio Feteira a.feteira@shu.ac.uk
DTA Programme	DTA Energy
Project title	Environmentally friendly Pb-free ceramics for energy storage

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Page 2 – Project Description

Scientific Excellence (500 words)	Materials exhibiting high energy and power density are currently needed to meet the growing power supply demand of portable electronics, electrical vehicles and other energy storage devices. In comparison to other energy storage devices (such as fuel cells and batteries), dielectric capacitors are receiving great deal of attention for advanced pulsed power due to their high-power density and quick charge-discharge rate. In general, there are three kinds of materials used in capacitors: linear dielectrics, anti-ferroelectrics (AFE) and ferroelectrics (FE). To achieve both high recoverable energy (W_{rec}) and efficiency (η), materials should exhibit large maximum polarisation (P_{max}), small remnant polarisation (P_r) and high electric breakdown strength (BDS). Often the latter is a limiting parameter, due to both intrinsic and extrinsic reasons. Pb-based AFE/FE already proved to exhibit good energy-storage properties, because of their inherently high polarisation. For example, $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$-$KNbO_3$ (BNT-BT-KN) ceramics can reach a W_{rec} of 1.72 J/cm^3. A very high BDS (300~400 kV/cm) was achieved in $K_{0.5}N_{0.5}NbO_3$-based ceramics by controlling grain growth and W_{rec} reached ~ 4 J/cm^3. Recently a multinational research team, including Dr. Feteira from Sheffield Hallam University, reported an ultrahigh discharge energy density (10.5 J/cm^3) and efficiency (η = 87%) in doped $BiFeO_3$–$BaTiO_3$ ceramic multilayers by achieving an electrically rather than chemically homogeneous microstructure. These multilayers exhibited a BDS greater than 700 kV/cm, combined with a maximum polarisation of 35 μC/cm^2. A systematic and comprehensive study that unveils the underlying mechanisms that control energy storage in ferroelectrics is still lacking. Indeed, the ability to understand how to tailor the energy storage performance

	characteristics of ferroelectrics while maintaining their naturally high polarisation is of paramount importance, if these materials are to be deployed into commercial applications. This is the main objective of this research proposal.
Aim (400 words)	*Aim* Develop an energy storage prototype with a recoverable energy density greater than 15 J/cm^3 based in BNT/BKT/BT ceramics. BNT-based ceramics exhibit a ferroelectric-to-relaxor (FE-RE) phase transition at ~100°C. Doping may be used to shift the FE-RE to lower temperatures thereby leading to a relaxor state at room temperature exhibiting enhanced energy storage. This combined with microstructural engineering may be employed to produce ceramics with greater BDS and high polarisation, thereby with enhanced energy storage characteristics. *Methodology and Innovations* (I) <u>Computer modelling</u> First, an innovative approach based on computer modelling using first principle calculations will be carried out as a screening approach to identify the most efficient dopants and their impact on crystal-chemistry. The CASTEP code will employed for this purpose. Using density functional theory, a wide range of properties can be simulated including structure at the atomic level, vibrational properties, electronic response properties and band structures. *(II)* *<u>Materials preparation</u>* Subsequently, the most promising candidates will be prepared by the standard solid-state reaction route. Firing under different atmospheres will be carried out. Crystal structure and purity will be characterised by X-ray

	diffraction, scanning electron microscopy, Raman spectroscopy, transmission electron microscopy. The latter will be employed to characterise the sub-grain microstructure. AC impedance will be employed to characterise the electrical microstructure. Polarisation will be measured under increasing electrical fields up to 200°C. Beamtime applications will be submitted to Diamond, in order to carry out diffraction experiments under applied electric field. Spark plasma sintering will be employed in selected compositions to evaluate its impact on the energy storage performance. *(III)* *<u>Device prototyping</u>* Multilayer devices will be fabricated by tape casting using selected compositions. Different electrodes materials will be tested. Throughout the research programme, the student will work closely with the industrial partners, to design devices, in order to improve their energy storage performance. Electrical fatigue measurements will be carried at different temperatures. Leakage current will me measured also at different temperatures. The most promising composition will be used to fabricate thin film device by spin coating.
Strategic Relevance (300 words)	Historically, UK has been internationally-leading in functional ceramics and inorganics research thanks to significant and sustained investments by the EPSRC and the Technologies Strategy Board. The current portfolio of £51 million represents 1.06 per cent of the total EPSRC portfolio. The specific area of materials for energy is currently funded at a level of £14 million. This level of investment it is to be maintained and therefore corroborates the importance of this research area in the EPSRC's strategic plan. This project is focused in clean energy, specifically in materials for energy storage.

	Currently, this is a research priority in both the UK, EU and US. The European Science Foundation Materials Science and the Engineering Expert Committee (ESF MatSEEC) report into 'Materials for Key Enabling Technologies emphasises the importance of maintaining support for continued research into the synthesis and discovery of new materials systems. The US department of Energy (DoE) also identified a so-called "*control age*", where research is about controlling functions through structure and composition - this strategy is at the heart of this PhD proposal. There is also a burgeoning segment of industry which is interested in innovative alternative technologies for energy storage – there is little doubt that this economic sector will develop in volume and value as global industrialisation places increasing demands on energy generation and storage. Finally, researchers working in materials for renewable energy production are probably the smallest group of beneficiaries, but are those that will engage most immediately with the research set out here. Hereafter specific areas of impact are addressed. Hence, the research outputs of the project will promote a swift advance in the field of energy storage technologies using ferroelectrics. The results will appear in high impact and widely read journals.
Interdisciplinarity and fit with DTA3	The student will benefit from supervision from an interdisciplinary team with expertise in ceramics and solid-state chemistry (Feteira), computer simulation (Ostler) and prototype fabrication (Sterianou), and from close collaboration with academic and industrial collaborators. The student will gain a theoretical understanding of materials properties using first-principle calculations, but will also develop experimental skills in synthesis, advanced characterisation techniques and fabrication of prototypes.

	In summary, the student will be equipped with the skills and experience to tackle global energy challenges. In addition, a fully successful outcome for the proposed research will be commensurate with Advanced Materials, RSC or ACS publications. The work will be presented a specialist conferences attended by both academics and industrialist. In summary, this project will increase the awareness on the multifunctionality exhibited by ferroelectric materials among different communities, such as electronic engineers, physicists, solid-state chemists, end-users and manufacturers. Another research community that will benefit from the results of the proposed research are modellers who use first principle calculations to predict physical properties of ferroelectrics. Basically, they will have experimental data either to validate their models or to improve their robustness. In summary, this PhD project is well aligned with the ethos of the DTA3, because of its interdisciplinary and industry focus.
Industrial Relevance (300 words)	The student will collaborate with Ionix Advanced Technologies Ltd a local SME but also with a major European manufacturer of passive electronic components (contact deliberately omitted from this application). As the project progresses, the student will have the opportunity to visit these industrial partners to learn about ceramic processing, to test the efficiency of prototypes and compare that to existing products. The companies will offer guidance on the transfer of the materials developed into efficient prototypes. collaborations, the student will have access to expertise and research facilities, which if necessary, will provide invaluable support to successfully complete the proposed PhD project. **Austria**: Dr. Marco Deluca (Materials Center Leoben) is long-term collaborator of Dr. Feteira. He was recently awarded an **ERC consolidator grant** in energy storage thin

	films. In the past, he hosted visiting PhD students supervised by Dr. Feteira and provided support in Raman spectroscopy. The student will visit Dr. Deluca to fabricate thin film devices, which may afford even higher energy densities. TDK EPC, the largest European manufacturer of passive ceramic components, offers placements in specific areas. **Spain**: Dr. Miguel Alguero (Institute of Materials de Madrid), is a current collaborator of Dr. Feteira. He is a senior researcher working in ferroelectrics. Selected samples will be sent to Dr. Alguero for spark plasma sintering. **China:** Dr. Di Zhou (Xi'an Jiaotong University). Selected samples will be sent for measurement of the time dependence of the discharge energy density. There will be opportunities to undertake short term scientific missions under the auspices of the EU CostAction CA17123-MAGNETOFON, for which Dr Ostler is a committee member.
Economic and Societal Impact (300 words)	This PhD research proposal relates to the realisation of affordable, clean and sustainable storage of energy. It is, therefore, highly pertinent to a wide range of real-world constituencies and potential beneficiaries. For example, members of the general public will be interested in economic benefits and environmental considerations whilst policy makers will focus more on the potential for improved energy security and reliability as well as contributions to international legal commitments on greenhouse emissions. *Economic impact* Moreover, the advanced ceramics and devices manufacture sector contributes with ~ £3 billion per year to the UK's economy, and represents 25% of the total EU production. The proposed project is framed around current energy challenges and the suggested approach is set across important pillars of the both EU and UK's government Industrial Strategy, such as innovative solutions for energy

	harvesting and storage in terms of new materials, training of highly skilled professionals to support the UK industry, direct support of UK businesses, which ultimately will enhance the research capability in a very important sector of the UK economy. The development of a new technology will bring economic benefits, as it increases EU and UK competitiveness in a key industrial area. It is important to stress that the global energy storage market is expected to reach $296 billion by 2024, according to a new report from Zion Market Research. *Societal impact* First, a new energy storage technology based in ferroelectric materials will support the successful implementation of clean energy. This will have an immediate impact in the improvement of the quality of life and on the environment. Second, the student will emerge as an internationally-connected, independent researcher with interdisciplinary and inter-sectoral skills and experience, ready for industrial employment in EU. Hence, this project provides the ideal platform to train the engineers of the future.

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Page 3 – Admission Requirements

Specific Admission Requirements	A graduate with 1st class or 2.1 degree in materials science, chemistry or physics will be most suitable for this project. An MSc. Degree will be an added advantage.
Minimum IELTS score	An overall IELTS score of 7.0 or above, with at least 6.5 in each component or an accepted equivalent

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