Thermoelectric Roadmap
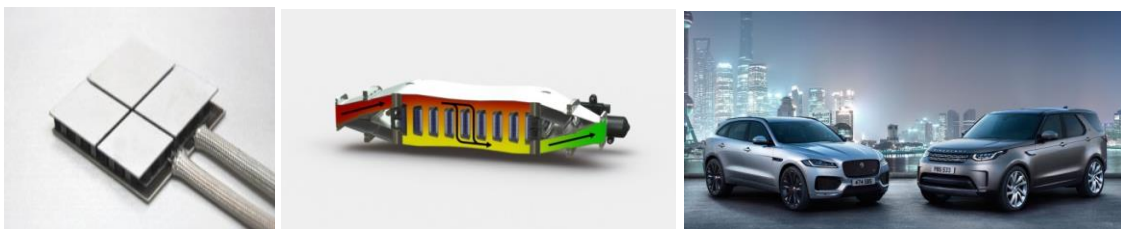
Energy Harvesting From Waste Heat

Prepared by

EPSRC Thermoelectric Network UK

May 2018

Foreword

The growing concern about CO_2 emissions, global warming and energy supplies over the past two decades has focussed attention on alternative, clean methods of power generation. Thermoelectric methods offer the benefit of a solid-state construction and allow the energy recovery solution to be readily adapted to the underlying process. Applications are as diverse as automotive, marine, aerospace, medical and the Internet of Things. Thermoelectric devices can also provide effective thermal management, including microelectronics and battery conditioning in electric vehicles, and refrigeration in an all solid-state device. Solid-state thermoelectric generators have been used effectively in niche applications such as satellite missions for over 50 years. There are now considerable opportunities to use thermoelectrics in a wide variety of domestic and industrial applications, including off-grid generation of electricity. However, to exploit thermoelectrics fully as energy harvesters in the different environments requires the development of new thermoelectric materials with enhanced performance over wider temperature ranges, along with high performance modules and systems.

The UK has a growing thermoelectric community, spanning all aspects of the development supply chain from modelling to materials to engineering, with good links between academe and industry. If the UK is to reap the benefits of the initial developments there should be investment and support for a new generation of thermoelectric materials that exploits the synergies between experimental and computational expertise, novel device architectures, associated novel manufacturing and materials preparation techniques and system integration.

This Thermoelectric Roadmap has been prepared by members of the EPSRC Thermoelectric Network. The contributions of the UK based members and overseas colleagues are gratefully acknowledged.

Editors

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1. EXECUTIVE SUMMARY AND CONCLUSIONS

1.1. Challenges and opportunities for Thermoelectric Devices

All machines from jet engines to microprocessors generate heat, as do manufacturing processes ranging from steel to food production. For example, up to 60% of energy in the internal combustion engine is rejected as heat (with transportation already recognised as a significant source of CO_2 emissions), and 8% of the UK's current greenhouse gas emissions are from heavy duty vehicles, a percentage which is predicted to increase to 30% as other sectors reduce emissions. Thermoelectric generators (TEGs) are solid-state devices that convert a heat flux directly into electrical power and therefore have the potential to offer a simple, compact route to power generation. TEGs can be developed to generate electrical power in almost every industrial sector and exploited to power devices, ranging from medical to building monitoring, and the Internet of things. The challenges are to develop new materials that continue to offer higher power output, while matching TE solutions to the wide range of applications that would benefit from energy harvesting.

The key points for the UK are:

(i) **Thermoelectrics are ideally placed to respond to the Grand Challenges of Sustainability and Resilience.**

(ii) **Thermoelectrics need to be included in proposal calls from Innovate and RCUK related to energy conversion/conservation themes**

(iii) **The UK has vast amounts of waste heat that can exploited** for energy recovery in transportation, marine and industrial sectors. Applications of thermoelectric (TE) technology range from microwatts to tens/hundreds kW, and potentially to MW.

(iv) **With the move from Internal Combustion Engines to hybrid and full electric vehicles over the next 20 years TE generators are capable of playing a significant role in all three forms of technology.** A robust thermoelectric community should be a high-tech UK asset for automobile manufacture.

(v) **Improved waste heat harvesting and recovery**, and more efficient cooling, offer significant **opportunities to reduce energy usage and CO_2 emissions**.

(vi) **The UK industrial sector is not fully exploiting the strong UK academic base in thermoelectrics**. There is a need to capitalise on the benefits of fully linking academic and industrial partners, and also to exploit the synergies between those working in materials, modelling, devices and applications. Effective funding is vitally important for strengthening the UK R&D community.

(vii) **There is a critical requirement for new materials** to be created as large scale applications require earth-abundant components. The discovery of new materials requires a concerted research effort.

(viii) **The UK has the supply chain to develop, manufacture and integrate thermoelectric devices** into a broad range of end-user sectors such as transportation, aerospace, construction, energy, retail and consumer products, all with global market potential.

(ix) **There is a need to embrace new state-of-the-art manufacturing techniques** to drive down the cost through high-volume manufacturing to widen the application base.

(x) **The significant investment elsewhere** puts the UK at risk of falling behind other European (e.g. Germany) and Asian (Japan, China) countries in the application of thermoelectric technology.

(xi) **To enable the UK to reap the benefits from initial developments and be able to exploit the growing market and opportunities for thermoelectrics it is recommended that there should be investment and support for a new generation of thermoelectric materials that exploits the synergies between experimental and computational expertise, novel device architectures, associated novel manufacturing and materials preparation techniques and system integration.**

2. INTRODUCTION

2.1 Energy and Power Generation

2.1.1 Energy and greenhouse gases

The Paris climate agreement of 2015 [1] on energy has the objectives to reduce greenhouse gas emissions by at least 20% compared to 1990 levels (see Figure 1) or by 30%, if the conditions are right (provided that other developed countries commit themselves to comparable emission reductions and that developing countries contribute adequately according to their responsibilities and respective capabilities); to increase the share of renewable energy sources in our final energy consumption to 20%; and to achieve a 20% increase in energy efficiency.
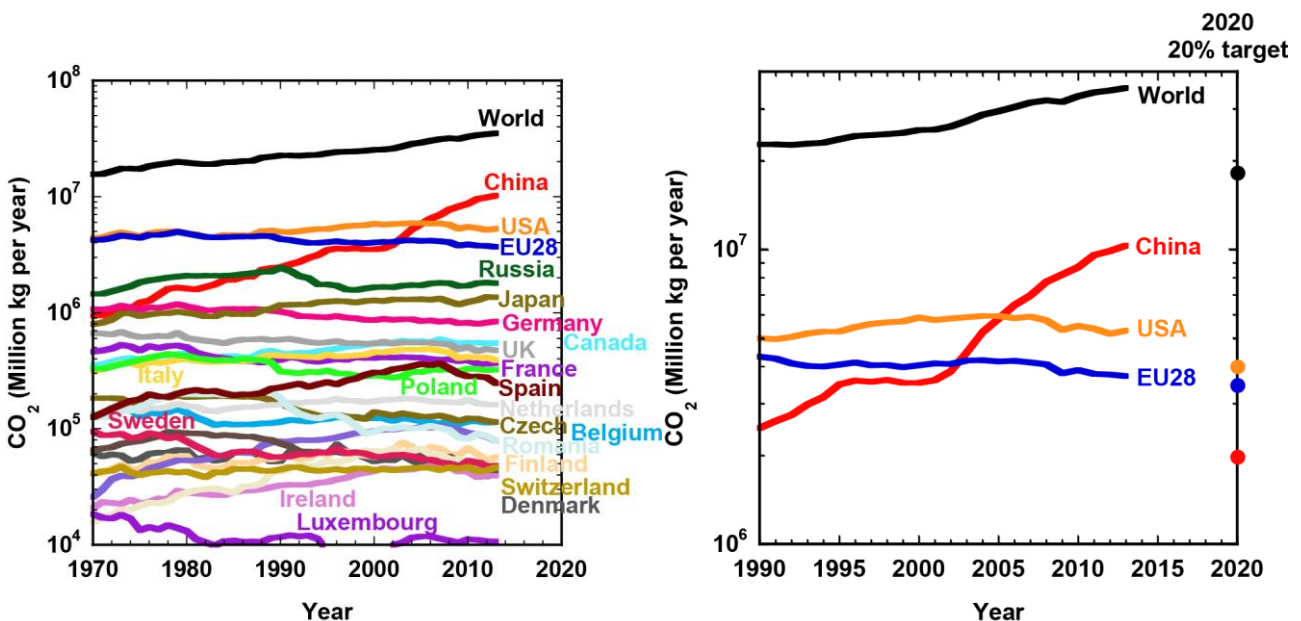
Figure 1: Left – The CO_2 emissions per year for EU 28 countries compared to major economies around the world; Right – the three major world economies and their proposed 20% reduction of CO_2 emissions of 1990 levels for 2020 [2].

The UK Climate Change Act (2008) sets a target of 80% reduction in CO_2 emissions by 2050, while the EU target is a 20% improvement in energy efficiency by 2020. Recent estimates are that *ca*. 37% of greenhouse gas (GHG) emissions are from the power generating sector with a further 17% (marginally less than the total for transportation including automotive) coming from manufacturing industries, with energy-intensive industries such as steel making being the biggest contributor.

There is enormous potential to make significant efficiency savings in these sectors by recovering useful energy from waste heat, reducing the demand for externally supplied electrical power and the greenhouse gas emissions that arise from its generation.

2.1.2 Heat Recovery and Cooling: The scale of the challenges – Waste Heat and Cooling

All machines from jet engines to microprocessors generate heat, as do manufacturing processes ranging from steel to food production. For example, up to 60% of energy in the internal combustion engine is wasted as heat (with transportation already noted above as a significant source of CO_2 emissions), and 8% of the UK's current greenhouse gas (GHG) emissions are from heavy duty vehicles, a percentage which is predicted to increase to 30% as other sectors reduce emissions [3].

An analysis of industrial waste heat [3] (Fig. 2) reveals that 80% of industrial waste heat is released as a heated gas at temperatures between 373 and 535 K. Removal of heat is frequently a priority in cooling of electronics, computer warehouses and in air conditioning. The latter is a major consumer of energy (around 10% across Europe), as is chilling of food where an estimated 29% of a typical hypermarket energy is used in chillers [4].

Industrial waste heat in Japan
2.72×10^{14} kcal per year
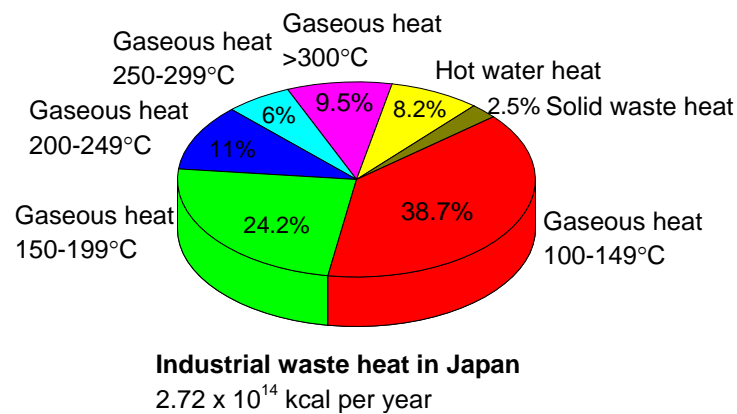
Figure 2: Waste Heat Distribution for Industry [3]

Conventional methods to convert heat energy use rotating 'Rankine cycle' machinery (e.g. pumps or turbines) but can be difficult to scale efficiently and require maintenance. Waste heat and inefficient cooling represent unnecessary GHG emissions. Recovered energy is generally used to lower the associated system power input, but waste heat energy is increasingly being investigated for a range of applications industrial scale processes to the powering of wireless sensors, relevant for the internet of things (IoT). Estimates of the UK's waste heat inventory are difficult to compile, but energy consumption by sector (illustrated in Figure 3) indicates that heat recovery in transportation applications (including road, commercial, public and private, rail and marine) would be especially attractive.
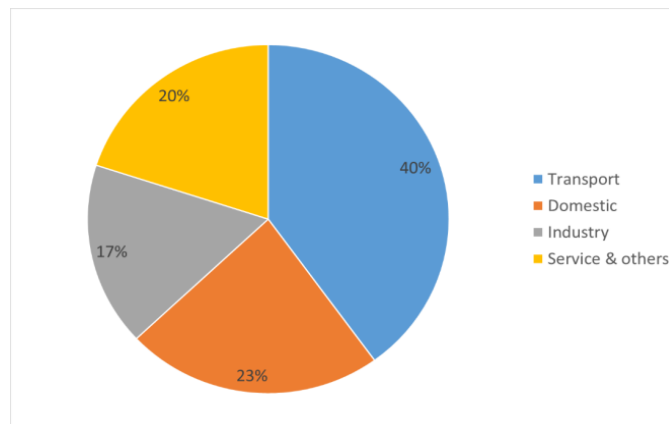
Figure 3: UK energy consumption by sector [5]

2.1.3 Benefits of the solid state approach using thermoelectrics

Thermoelectric generators (TEGs) are solid-state devices that convert a heat flux directly into electrical power and therefore have the potential to offer a simple, compact solution. TEGs can also operate in reverse and effect cooling upon passage of an electric current (known as the Peltier effect). TEGs are made mostly from semiconducting, inorganic compounds. They have no moving parts and can be retrofitted to existing waste heat sources or integrated into the total system. They are readily scalable from electronic chip-size to tens/hundreds kW units. The operating conditions of the application determine the type of materials used and the device design. They can be very reliable and are the power-conversion source of choice in hostile environments such as remote pumping stations for oil pipelines and space satellites. They also have considerable potential for off-grid electricity generation.

2.2   The Seebeck and Peltier Effects

The thermoelectric phenomenon is the conversion of heat energy into electrical energy, and vice versa, using solid-state materials. If a temperature gradient (dT) exists across two dissimilar materials (a and b) which are in contact then a potential difference (dV) is generated between the free ends of the circuit. This is described by the Seebeck effect. The Seebeck coefficient (α) is defined by:

$$\alpha_{ab} = \frac{dV}{dT} \tag{1}$$

If the generated dV is applied across some external electrical resistance a current will flow, and the Seebeck effect provides the basis of a power generation mode; the reverse process of passing a current through a thermoelectric to extract heat is the basis of the refrigeration mode (Fig 4).
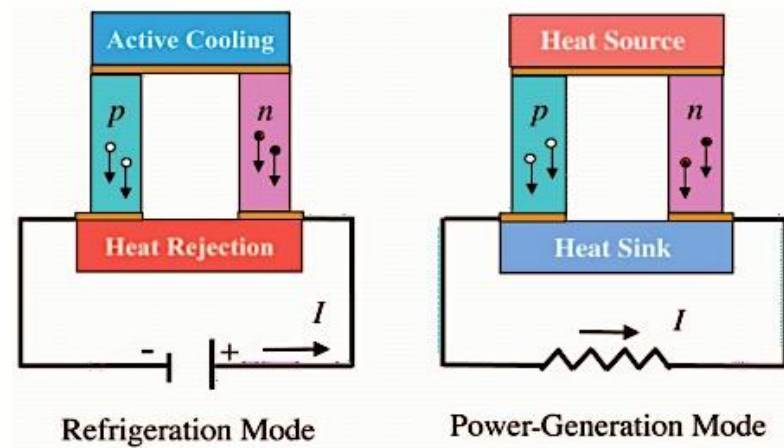
Figure 4: A representation of the TE effect in (left) a Peltier cooler and (right) a TE generator. Charge carriers move from one end of the thermocouple, carrying entropy and heat towards the other end. Both n- and p-type materials are necessary for a complete device

The efficiency of a thermoelectric device is directly related to the performance of the semiconducting materials from which it is composed. The materials' performance is embodied in a dimensionless figure of merit, ZT, incorporating the Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (κ), which may be formulated as:

$$ZT = \frac{S^2 \sigma T}{\kappa} \qquad (2)$$

The thermal conductivity has contributions both from charge carriers (κ_e) and lattice vibrations (κ_L). High performance requires a large Seebeck coefficient and low thermal conductivity, characteristic of non-metallic systems, to be combined with a high electrical conductivity, more usually found in metallic phases. Consequently S and κ cannot be optimized independently, presenting a challenge in the design of high-performance materials. The best compromise is generally found in semiconducting materials with charge carrier densities in the range 10^{19}-10^{20} cm^{-3}. Device efficiency (η) may be approximated by:

$$\eta = \frac{T_h - T_c}{T_h} \left[\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT} + \frac{T_c}{T_h}} \right] \qquad (3)$$

where T_h/T_c is the temperature of the hot/cold junction and ZT is the average for the device over the temperature range T_c to T_h. An increase in the average ZT over the temperature range of operation of the device has a more marked impact on efficiency than merely increasing the maximum figure of merit of the component semiconductors.

2.3   Designing for Thermoelectric Applications

The most commonly used technique to characterize thermoelectric generators (TEGs) at the module level involves maintaining a constant temperature gradient across the device while varying the electrical load conditions. Typically a manufacturer will provide a set of curves for different temperature differences (50 °C, 100 °C, 200 °C, 300 °C, etc.) showing the variation in output power and load voltage with output current. This "constant temperature" approach disregards the variation of the heat flux through the TEG due to the parasitic Peltier effect which is proportional to the load current. From a designer's perspective it is usually desirable to operate the TEG system at its maximum power point (MPP), i.e., when the load resistance is matched to that of the module; the condition defined by the maximum power transfer theorem. However, this condition is formed from a purely electrical point of view and it does not consider any thermal interactions in the TEG system that may be influenced by the Peltier contribution to the heat flow.

Typically the hot-side energy source available for TEG application is "limited" waste heat, therefore the temperature gradient across the module will not remain constant. This means that the conditions used to characterize TE modules are not comparable with the operational conditions of the TEG when integrated in a real system. Because of this, there may be significant mismatches in the TEG performance predictions between characterization and application and the inclusion of the Peltier effect on the system performance is essential for determination of actual system operation.

If such a "*constant heat*" characterization is performed with the conditions of a TEG integrated in an application the impact of the parasitic Peltier effect on power generation can be quantified and then reduced by operating the module at a lower current. This will lead to an increase in the temperature

gradient across the module and hence also overall power generation (since power is proportional to V^2) compared to the values predicted using only the maximum power transfer theorem condition.

Generally some form of electrical conditioning is required between the variable output voltage of the TEG and the fixed voltage requirement of the load. This is accomplished using a power converter which attempts to extract the maximum amount of energy from the TEG module. Commonly used "maximum power point tracking" (MPPT) algorithms are implemented in TEG power converter systems. The algorithm must be able to simultaneously accommodate the rapid electrical responses and the much slower thermal responses, having very different time constants. Further, in order to implement the latest high performance algorithms, the power converter requires information of the TEG temperature.

In order to get the best possible performance from the TEG module the correct mounting of the device in the thermal system is essential. The following general guidelines are widely accepted:

- The hot and cold-side heat exchangers should be flat (< 0.05 mm) and polished for heat transfer (roughness < 1μm). Heat exchanger surfaces should be parallel to one another.

- The recommended clamping pressure depends on the thermal transfer compound and is 1.1 MPa (175 kg for a 40x40 mm module) for graphite. Achieving the required pressure can be challenging for weight-sensitive applications (e.g. automotive).

- Graphite coating on the module faces offers the best long-term performance since it does not dry out at high temperature. Modules are available without a graphite coating if thermal grease is to be used. This offers a slight (< 3%) reduction in output power but with approximately half the clamping pressure.

- Gap fillers with a thermal conductivity of > 2 W/m.K are not recommended and are likely to lead to significantly reduced output power from the system.

2.4 Inorganic Materials

2.4.1 Factors in materials selection

Current commercial TE devices are composed of Bi_2Te_3 appropriately doped to produce the required n- and p-type variants. Whilst offering good performance at temperatures close to ambient, there are two principal factors associated with Bi_2Te_3 that limit future applications.

Abundance: Tellurium is a relatively scarce element, with a terrestrial abundance of *ca.* 1 ppb. A recent analysis, (*Periodic Table of Endangered Elements*) conducted by the Chemistry Innovation KTN identifies tellurium as one of the top 9 "at risk elements". Tellurium is obtained (but not always separated) as a by-product of copper ores. Therefore its availability is also limited. Coupled with a rising demand for tellurium from other technologies, including photovoltaic, these factors provide a strong driver for the development of new TE materials comprised of earth-abundant elements.

Performance: Bi_2Te_3-based devices exhibit a maximum ZT that approaches unity at temperatures in the range $350 \leq T/K \leq 450$. This equates to an efficiency of the order of 2-3% for energy harvesting applications. At higher temperatures, the figure of merit falls off markedly and Bi_2Te_3 melts at 853 K. Given the wide range

of hot-side temperatures for energy harvesting applications, there is a need to develop a portfolio of materials, with thermoelectric properties optimized to the temperature range of the application.

In creating new materials for the applications outlined in Section 4 a number of additional materials constraints apply. These include:

Materials Stability: Under operating conditions, TE devices are subjected to significant temperature gradients for extended periods. The component materials need to be stable with respect to both oxidation and sublimation under such conditions. These demands increase as the hot side temperature is raised. Given the inherent instability with respect to aerial oxidation of many advanced TE materials, the complementary development of protective coatings is likely to be a priority.

Scalable Production: Many of the applications identified in Section 4 will require high production volumes of TE devices. Conventional metallurgy is unlikely to provide the large quantities of material required, particularly where protective (inert gas or vacuum) environments are required during production. Mechanochemical alloying is likely to play an increasing role in scalable production of TEs, whilst solution-based methods offer an attractive alternative in favourable cases.

Processability of the Powders: Whilst Bi_2Te_3 materials are produced by a melt based process, many of the advanced thermoelectric materials recently discovered do not melt congruently. Such materials are therefore generally produced in powder form. Consequently device fabrication requires consolidation of the powders into ingots, from which thermoelements may be cut. Consolidation methods are required that produce mechanically-robust ingots with the appropriate microstructure. Moreover, the methodology needs to be scalable. This will require the extension of hot pressing and Spark Plasma Sintering methods to larger ingots and the application of novel manufacturing methods, developed in other sectors, including 3D printing, aerosol deposition and capacitive discharge sintering.

Availability of Compatible n- and p-type Materials: Thermoelectric module performance is determined by the thermoelectric properties of the n- and p-type materials of which it is composed. High performance requires both n- and p-type legs to exhibit comparable figures of merit. The availability of complementary n- or p-type materials frequently imposes a barrier to the construction of next-generation modules. In addition to well-matched physical properties, the thermal expansion coefficients of the n- and p-type materials need to be comparable in order to avoid the introduction of stresses under the operating conditions of the device. Flexible contacts may offer a way of alleviating this problem.

2.4.2 Materials Design Strategies

Advances in the understanding of the relationship between chemical composition, structure (over multiple length scales) and thermoelectric properties has led to the emergence of a number of materials design strategies that will guide the search for new high performance materials. Many of these seek to achieve a degree of separation between the electrical and thermal contributions to the figure of merit.

These strategies include:

Phonon-Glass Electron Crystal (PGEC): Localized vibrational modes of weakly bound atoms introduced into vacant sites within a semiconducting framework, serve to scatter heat-carrying phonons. This provides a

means of reducing the lattice component of the thermal conductivity (κ_L) without impacting negatively on the electrical transport properties of the framework.

Nanoinclusions and Nanocomposites: Compositional inhomogeneities within a semiconducting matrix can create endotaxially embedded nanoinclusions. These scatter acoustic phonons with no significant impact on the charge carriers. A variant of this method is the introduction of nanoparticles of a second phase to form a physical mixture with a thermoelectric material of proven performance, prior to consolidation. This can produce significant reductions in thermal conductivity.

Grain Boundary Engineering: The increasing realization of the importance of microstructure on thermoelectric properties has led to significant efforts to manipulate the scattering of heat-carrying phonons at grain boundaries, including selective precipitation of a second phase at grain boundaries. Dense dislocation arrays formed at low-energy grain boundaries scatters mid-frequency phonons with a minimal effect on electron transport.

Band Structure Modification: Improvements in thermoelectric power factor have been targeted through band engineering to increase the valley degeneracy, N_v. The resulting increase in carrier mobility enhances the TE properties. High N_v is favoured by high symmetry and a small energy separation between bands of different character: chemical substitution provides a means of tuning this separation. In an alternative approach, the introduction of post-transition-series impurity atoms can lead to perturbations in the density of states of a semiconductor through the creation of resonant states, which leads to significant enhancements in the figure of merit.

Phonon-Liquid-Electron-Crystal (PLEC): At elevated temperatures, highly mobile ions can assume a liquid like state within an otherwise rigid crystalline matrix. The resulting disorder induces significant reductions in the lattice contribution to the thermal conductivity (κ_L), without impacting negatively on the electrical properties. However, concerns that the high ionic mobility can lead to migration of the mobile species to the electrodes and hence degradation of the material, as a result of the potential difference created, need to be addressed if PLECs are to be implemented.

Energy Filtering: Carriers with a mean energy substantially below the Fermi level are "filtered" by potential barriers and hence do not contribute to transport. The filtering results in electrical conductivity reduction and Seebeck coefficient improvement. The former can be more than compensated for by the latter when the potential barrier is only a few k_BT higher than the Fermi level, thereby resulting in an enhanced power factor. It is effective when the distance between the potential barriers are comparable to the carrier mean free path.

Low-Dimensionality: Structures of reduced dimensionality exhibit a more highly structured Density of States (DOS) than conventional bulk 3D materials. Theoretical work indicates that significant enhancements in the Seebeck coefficient may be realised by tuning the Fermi level to sharp discontinuities in the DOS. The increased scattering of phonons resulting from the larger number of interfaces associated with low dimensionality has perhaps a greater beneficial impact on thermoelectric performance.

These design strategies can be applied to a wide range of materials, with properties that are matched to the different temperatures of operation. The emphasis on materials containing earth-abundant elements will

grow. Increasingly, we are likely to see a combination of approaches adopted that simultaneously address the electronic and thermal contributions to the figure of merit. The range of advanced TE materials includes:

2.4.3 Bulk Inorganic Materials

Chalcogenides: These are amongst the most studied TE materials. In addition to Bi_2Te_3 at the heart of commercial modules, PbTe has been considered a candidate for high-temperature operation. Recent work has focused on endotaxially embedded nanoinclusions in PbTe, exemplified by the LAST-m phases, leading to figures of merit in excess of 1.5 at high temperatures. The need for alternatives containing earth-abundant elements has led to figures of merit approaching unity for the corresponding binary selenides and sulphides. Environmental concerns surrounding lead have motivated extension to the tin congeners. SnSe exhibits an exceptional figure-of-merit, although concerns have been expressed about the reproducibility of the result. Chalcogenides for operation in the mid-range of temperatures include a variety of layered and pseudo-layered materials for which $ZT \approx 0.5$ may be attained.

Drawing inspiration from the world of minerals, synthetic derivatives of tetrahedrite have been shown to exhibit $ZT \approx 1.0$ at 700K. Mineral chemistry may provide a rich vein of potential thermoelectric materials in the future. Work on synthetic derivatives has already included those of shandites, colusites, argyrodites and bornites.

PLECs: The observation of $ZT = 1.5$ at 1000 K in the superionic conductor $Cu_{2-x}Se$ has stimulated work on copper-containing chalcogenides more generally. In particular, efforts are being made to create materials in which substantial reductions in thermal conductivity arising from copper-ion mobility can be achieved without the detrimental effects on device performance that arise from ionic conductivity.

Oxides: Metal oxides offer advantages for high-temperature applications, owing to their stability in air at elevated temperatures and ready abundance. Their ionic nature results in relatively low electrical conductivity. The challenge is to improve the electrical properties without impacting negatively on thermal conductivity. Typically this involves doping a stoichiometric phase. Substitution in the perovskite $SrTiO_3$ has been widely studied. The insights into composition-structure-property relationships that have emerged from wide-ranging investigations of perovskites for non-TE applications suggest considerable opportunities for the discovery of new TE phases. Other oxide TE phases include a range of layered cobaltites, the structures of many of which are incommensurate, which itself has a beneficial impact on thermal transport properties.

Oxy-chalcogenides: Mixed anion compounds have received limited attention as potential thermoelectrics. The differing bonding preferences of oxide and chalcogenide ions leads to ion segregation and the creation of two-dimensional building blocks. The more ionic oxide units favour low thermal conductivity, while covalency promotes high mobility semiconduction. Whilst the thermal conductivity is low, efforts are required to improve the electrical properties through chemical substitution. $ZT \approx 0.8$ has already been realised by judicious substitution. There is considerable scope for exploration of new structure types containing alternative oxide/chalcogenide building blocks to the fluorite/antifluorite that have formed the basis of the majority of investigations to date.

Skutterudites: This family of materials, derived from $CoSb_3$, represents a realization of the PGEC concept. The key feature of skutterudites is the presence of a large cavity, into which weakly bound guest species can be placed. In addition to effecting reductions of almost an order of magnitude in thermal conductivity,

through localised vibrational modes (termed rattling modes), guest species transfer electrons to the framework. Therefore optimization of the framework composition is often required in order to maximise the figure of merit. Filler atoms of different mass and size exhibit different resonance frequencies. Multiple filling scatters heat carrying phonons over a wider energy range, producing even greater reductions in thermal conductivity. The maximum figures of merit of singly filled materials exceed unity, whilst multiple filling leads to ZT = 1.7. The maximum figures of merit tend to occur at temperatures in the range $700 - 900$ K, making the materials candidates for power generation in the intermediate to high temperature range. This includes applications in the automotive sector. Chemical substitution can be used to produce both n- and p-type variants, providing chemically-compatible legs (thermoelements) for a device. At high temperatures, oxidation and/or sublimation of antimony may occur, leading to significant degradation of performance under the operating conditions of a device. The development of protective coatings should be a high priority to facilitate exploitation of skutterudite-based devices.

Intermetallics: Zintl phases possess complex crystal structures in which electron transfer between an electropositive species such as a rare-earth or alkaline earth atom and a complex anion of electronegative main-group elements confers salt-like characteristics. Investigation of the thermoelectric properties of Zintl phases is at a comparatively early stage. Initial results suggest that they are promising candidates for high temperature materials ($Yb_{14}MnS_{11}$ exhibits $ZT \approx 1$ at 1200 K for example) as the exceptionally low lattice thermal conductivity is sufficient to overcome performance limitations that would otherwise arise from a low electronic mobility.

Generally the maximum figures of merit are observed at high temperatures (> 1000 K). Synthesis is often challenging as high temperatures and extended reaction times are required: induction heating enabling synthesis to be carried out from the molten elements at ~ 2400 K. Narrow phase boundaries limit the accessible range of carrier concentrations, whilst the creation of chemically-compatible n- and p-type components can be problematical.

Clathrates: These intermetallic phases possess a cage-like structure of main-group metal atoms with electropositive species incorporated within the cage. In this respect they have parallels with skutterudites, whilst the bonding is described in terms of the Zintl concept analogous to the intermetallics outlined above. From a thermoelectric perspective, the important phases are those termed 'type I' of general formula A_8E_{46}, which includes those containing the more earth-abundant elements, silicon and aluminium. The materials are narrow band-gap semiconductors. The A cations exhibit rattling type vibrations and the materials offer another example of PGEC behaviour, with thermal conductivities typically below 2 W m^{-1} K^{-1}. Both n- and p-type clathrates may be prepared. Figures of merit for polycrystalline materials are typically in the range of ZT $= 0.7 - 0.9$, with higher values being attained for single crystals. The maximum figures of merit are achieved at $800 - 900$ K, making them suitable for energy recovery in the intermediate to high temperature range.

Half Heuslers: Bonding in the intermetallic half-Heusler compounds, X(YZ) where X, Y and Z are respectively an electropositive element, a transition-series element and a main-group element, can also be considered within the framework of Zintl compounds. Unusually from a thermoelectric perspective, the half-Heuslers exhibit relatively high thermal conductivities ($3 - 4$ W m^{-1} K^{-1}), which are compensated by large power factors (up to 6 mW m^{-1} K^{-2}) leading to figures of merit in the region of unity in the range $700 - 900$ K with suitable doping. The majority of high performance materials are n-type, although p-type behaviour has also been observed. There is significant scope to improve the thermoelectric performance by reducing the thermal

conductivity. Adoption of a hierarchical approach to phonon scattering across multiple length scales is necessary. Phase segregation can be induced during synthesis from high-temperature melts using an appropriate heating/cooling profile, thereby introducing compositional inhomogeneities, which have a beneficial effect on thermal conductivity. The existence of competing binary and Heusler phases can lead to uncertainties in composition, sample homogeneity and reproducibility and TE properties that are sensitively dependent on sample processing.

Si-Ge Alloys: Silicon is the second most abundant element in the earth's crust making TE materials based on silicon attractive candidates for large-scale implementation of the technology. However, the thermal conductivity of elemental silicon is extremely high (148 W m^{-1} K^{-1}), although it can be reduced through the addition of *ca*. 30% of germanium. Silicon-germanium alloys are used in radioisotope thermoelectric generators for deep-space probes. Both n- and p-type variants can be produced, with respective figures of merit reaching 1.0 and 0.7. Efforts to improve the thermoelectric performance of silicon have focused on reducing the thermal conductivity through methods such as nanocompositing with a second phase, or by grain size reduction to increase phonon scattering.

Nanostructuring leads to enhancements in the figures of merit; n- and p-type derivatives reaching ZT = 1.3 and 0.95 at very high temperatures (*ca*. 1200 K). In addition to the high temperatures required for maximum performance, the inclusion of the expensive element germanium significantly increases the material cost, to a level which is likely to be prohibitive to implementation in anything other than niche applications. Efforts are therefore required to reduce the germanium content in the alloys while retaining similar levels of performance.

Metal Silicides: The ready availability of silicon has led to an investigation of TE properties of materials in which it is combined with other earth-abundant elements. Alkaline earth silicides show promising n-type behaviour. Doping of Mg_2Si leads to ZT in the range 0.5 – 0.7, whilst band engineering through alloying with the corresponding stannide has raised the figure of merit to 1.3 at 700K. In addition to issues associated with fabrication, arising from the brittleness of the materials, the principal limitation on alkaline-earth silicides is the absence of a compatible p-type analogue that exhibits comparable performance over the same range of temperatures: lithium-doped $Mg_2(Si,Sn)$ being amongst the best with ZT = 0.5 at 750K. In the search for new high-performance materials, the net has widened to encompass transition-metal silicides. Manganese silicides, suitably doped with main-group or transition-series elements, exhibit a peak ZT = 0.4 - 0.6. Of the other transition-metal silicides investigated to date, rhenium silicide exhibits good n-type behaviour, although the cost of rhenium is likely to be prohibitive. Metal silicides are ripe for further exploration and optimisation, particularly through band engineering and nanostructuring.

Table 1: Thermoelectric Figures of Merit for Representative Examples of the Families of Thermoelectric Materials

TE Family	Representative Examples	n/p	Peak ZT	Temperature of Maximum ZT/K
Chalcogenides [6]	$Bi_2Te_{3-x}Se_x$	n	1.15	370
	$AgPb_{18}SbTe_{20}$	n	2.2	800
	$Pb_{0.96}Sr_{0.04}Te$ doped with Na	p	2.2	915
	$Cu_{10.5}NiZn_{0.5}Sb_4S_{13}$	p	1.03	723
	Cu_5FeS_4	p	0.55	543
Oxides [7]	$LaCrO_3$	p	0.14	1600
	$La_{0.15}Sr_{0.775}TiO_{3-\delta}$	n	0.41	973
	$Zn_{0.98}Al_{0.02}O$	n	0.3	1272
	$Ca_3Co_{3.9}Fe_{0.1}O_9$	p	0.39	1000
PLEC Phases [6]	$Cu_{2-x}Se$	p	1.5	1000
	$Cu_{2-x}S$	p	1.7	1000
	Cu_7PSe_6	p	0.35	575
Oxy-chalcogenides [6]	$Bi_{0.875}Ba_{0.125}CuSeO$	p	1.4	923
	$BiOCu_{0.975}Se$	p	0.81	923
	$Bi_{0.975}Cu_{0.975}SeO$	p	0.84	750
Skutterudites [8]	$Ba_{0.08}La_{0.05}Yb_{0.04}Co_4Sb_{12}$	n	1.7	850
	$Yb_{0.25}La_{0.60}Fe_{2.7}Co_{1.3}Sb_{12}$	p	0.99	700
Intermetallics [9]	$Yb_{14}MnSb_{11}$	p	1.04	1228
	$YbZn_{0.4}Cd_{1.6}Sb_2$	p	1.2	700
	Zn_4Sb_3	p	1.3	673
Clathrates [10]	$Ba_8Ge_{16}Ge_{30}$	n	1.35	900
	$Ba_8Ge_{16}Al_3Ge_{27}$	p	0.61	760
	$Yb_{0.5}Ba_{7.5}Ga_{16}Ge_{30}$	n	1.1	950
Half-Heuslers [11]	$TiNiSn$	n	0.4	775
	$Zr_{0.3}Hf_{0.65}Ta_{0.05}NiSn$	n	0.85	870
	$Hf_{0.44}Zr_{0.44}Ti_{0.12}CoSb_{0.8}Sn_{0.2}$	n	1.0	1073
Silicon-Germanium Alloys [12]	$Si_{0.8}Ge_{0.2}$ doped with P	n	1.3	1173
	$Si_{0.8}Ge_{0.2}$ doped with B	p	0.95	1223
Metal Silicides [12]	$Mg_2Sn_{0.7}Si_{0.3}$ doped with Sb	n	1.3	700
	$Mg_{1.86}Li_{0.14}Si_{0.3}Sn_{0.7}$	p	0.5	750
	$MnSi_x$ ($1.71 \leq x \leq 1.75$)	p	0.6	800

2.5   Organic thermoelectrics

2.5.1 Introduction

Organic thermoelectric materials (OTEs) are emerging candidates for TE applications. They are characterised by their low thermal conductivity, mechanical flexibility, elemental abundance and their solubility which enables manufacture by scalable printing techniques (inkjet, slot-die, roll-to-roll etc.). Whilst it seems unlikely in the near term OTE materials will replace inorganics in standard device architectures, they lend themselves towards certain non-conventional geometries and applications not accessible by incumbent technology.

The UK has a very vibrant research base in organic electronics both in universities and industry (CDT Ltd., FlexEnable, Merck, Flexink, Polyphotonix, Molecular Vision etc.), and a number of players are directing activities towards thermoelectrics.

2.5.2 Target Applications

Lower power factors (PFs) and ZT than their inorganic counterparts mean that organic OTEGs are candidates for low power applications near room temperature where their other properties are beneficial (flexibility, shock resistance, processability, sensing, biocompatibility, low toxicity etc.).

Two such application areas that have been identified are:

- Power sources for *Wireless Sensor Networks* and *Internet of Things* (minimum power requirements 70 µW; ΔT = 25 °C, operating temperature: 40 °C - 250 °C, area: 1-10 cm^2). ΔT for this application could come from water pipes and hot surfaces (Figure 5a).
- *Body-centred autonomous microelectronics* (minimum power requirements 70 µW; ΔT = 5 °C, operating temperature: 37 °C, output voltage: 10 mV, area: 1-10 cm^2). It is notable that IMEC, Belgium developed a wireless electroencephalography system with sub-microWatt power consumption that was powered by a TEG [13].

In addition *self-powered sensors* may also be realised where the OTE material used to generate power is also sensitive to pressure, temperature, humidity, biological markers etc. A self-powered dual temperature-pressure sensitive "e-skin" based on OTE materials is one example of this (Figure 5b [14]).

2.5.3 Current Materials and Properties

p-type. The current state-of-the-art for p-type OTEs is poly(3,4-ethylenedioxythiophene) (PEDOT) which has ZT of up to 0.4 when doped with polystyrene sulfonate (PSS) [15], Being air-stable and processable from water solution, PEDOT:PSS is compatible with industrial processes.

n-type. The current state-of–the-art n-type OTE are organometallic coordination polymers, in particular poly(Ni-ethylenetetrathiolate). These show PFs >400 µW·m^{-1}·K^{-2} and ZT of 0.30 at room-temperature. The material is air-stable, but non-soluble and so doesn't have the processing advantages offered by other organic materials.

Composites. The limiting parameter for organic thermoelectric materials is typically the electrical conductivity (σ < 1000 S cm^{-1} for OTE). Nonetheless organic materials can easily be processed with more conductive materials such as carbon nanotubes or graphene [16]. These can achieve significantly higher power factors (several 10s µW· m^{-1}·K^{-2}) at the expense of ZT [17] (i.e. for higher power devices with lower efficiency).
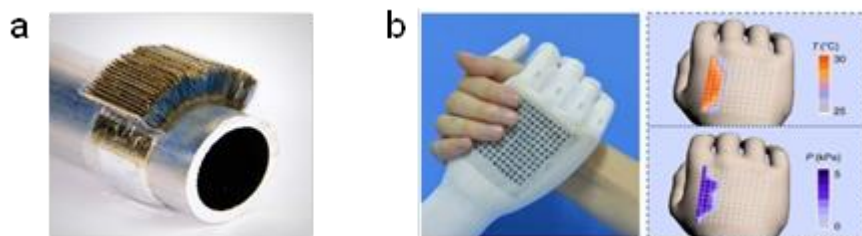

Figure 5: (a) A printed and folded OTEG wrapped around a hot water pipe (b) A self-powered dual pressure-temperature sensor patch on a prosthetic arm [14] . (www.otego.de).

2.6   Thin Film Thermoelectric Generators

Bi_2Te_3 and Sb_2Te_3 are the archetypal thermoelectric materials which have shown their worth for decades in radio isotope generators (RTG). They have the highest ZT values of any material in the temperature range of room temperature to about 200 °C and have a long track record of development and optimisation. An ideal sweet spot exists for these material types in thin film energy harvesting TE micro-generators for smart, possibly flexible, IoT applications including medical applications related to harvesting of body heat.

The figure of merit of thermoelectric materials ZT which determines their efficiency does not contain any geometrical parameters and thin film thermoelectrics could generate large amounts of energy. Furthermore, the possibility of nanoscale devices is theoretically predicted to lead to significant enhancement of the ZT value and experimental confirmation of the effects of quantum confinement is a key scientific driver. In terms of applications, a difficulty for thin film TEGs is to ensure that parasitic effects are minimized and that system performance approaches that for material and device properties. Due to the scales involved, the interfacial effects also play a large role. These can be beneficial, where direct deposition of TEs onto substrates leads to very good thermal coupling, or detrimental where interfacial reactions between substrate and TE during processing or use, decrease the thermal coupling.

In particular, thermal conductivity has to be lower than the ZT trade-offs suggest to ensure that the temperature drops over the TE material. Furthermore, the geometry can bring problems. Whereas for bulk TEGs, the TE legs are separated by air or other gasses, in thin film TEGs electrical insulators with considerable thermal conductivity might be required as substrates. Lastly the contacts to the metal connections, both electrically and thermally, have to be optimized to enable thin film TEGs to be of practical use in more than niche applications. Examples of thin film thermoelectrics are shown in Fig 6 and Fig 7.

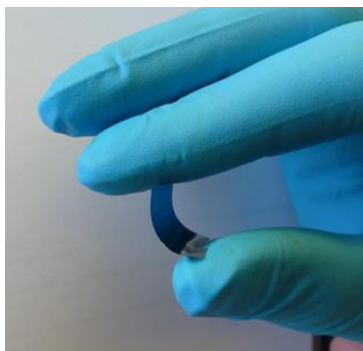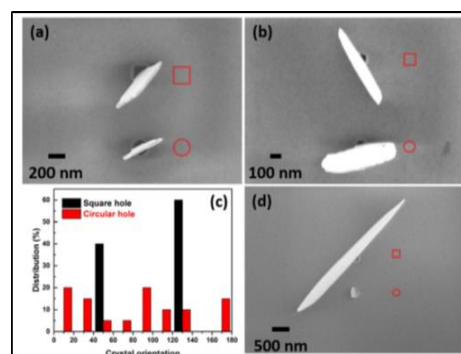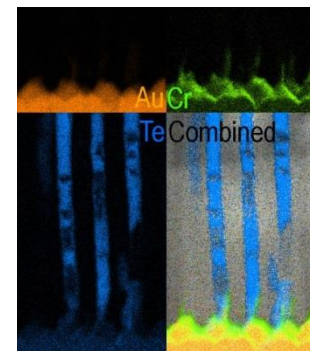**Figure 6**   **Figure 7a**   **Figure 7b**

Figure 6: Photograph of a piece of flexible, thin-film silicon (courtesy of Dr N Bennett, Heriot Watt University)

Figure 7: (a) Oriented Bi_2Te_3 nanosheets produced by selective chemical vapour deposition (b) Nanowires of Te (diameter 10nm) by supercritical fluid electrodeposition (courtesy of Prof K de Groot, University of Southampton)

3. MODULES

3.1   Device Manufacture Considerations

Architecture. Thermoelectric modules are typically arranged in the standard vertical or 'π' formation with n-type and p-type thermoelements or 'legs' arranged electrically in series and thermally in parallel (Figure 8). There are electrodes on the hot side and cold side with the material chosen dependent on the thermoelectric material used. Module design is typically defined by the leg length L and aspect ratio - the ratio r of the leg length to the leg cross sectional area A.

The other main arrangement of thermoelectric elements is the lateral formation which is typically used for flexible thin film module designs. There are other more experimental designs including annular; concentric rings arranged around a pipe for extracting waste heat energy; and 'stack', layers of thermoelectric sheet materials joined together (see Fig 8 for examples).
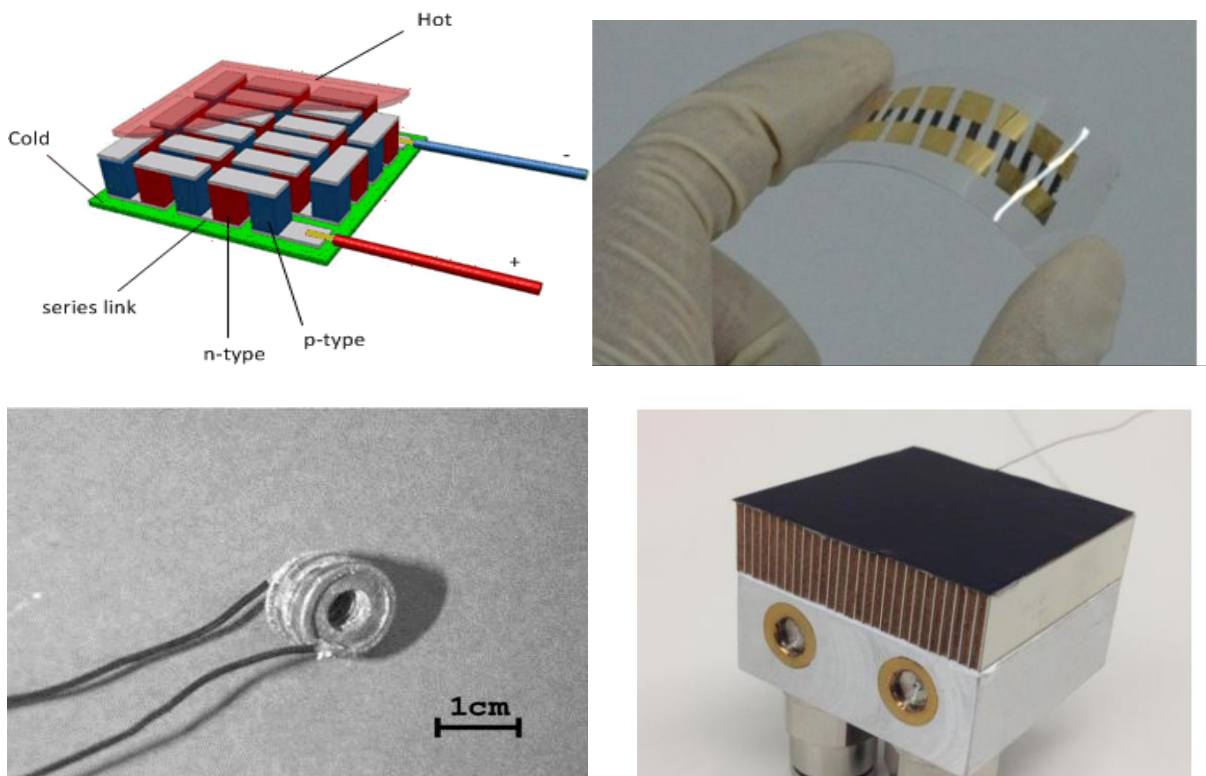
Annular structure   *Stack structure*

Figure 8: Arrangements of thermoelements: standard 'π' [18], flexible [19], annular structure [20], stack structure [21].

Module Geometry. This is an important consideration when designing a system for TE energy generation. If there is a plentiful source of heat energy available, then a low aspect ratio design with short legs can be utilised to maximise the power generated. This does however come at the expense of efficiency. If limited heat energy is available, a high aspect ratio design can be used to maximise efficiency at the expense of power generation. Another consideration is the power-to-material-volume ratio. If exotic materials with a limited abundance are used to create a module, it may be economically beneficial to reduce the volume of the legs whist maintaining the same aspect ratio so as to conserve the module performance. A balance must

be obtained, if the volume of the thermoelements is too small then thermal contact resistance and electrical resistance may start to impact on module power output and efficiency.

Electrically Insulating Substrate. Commercial bismuth telluride modules typically have top and bottom plates made from aluminium oxide but AlN/Si_3N_4 has also been used for niche applications. The substrate serves two purposes, (i) to isolate the thermoelement pairs and (ii) provide structural support of the legs within the module. Thin film organic/inorganic modules typically use novel substrates such polyimide films or anodized aluminium which allows printing of the module electrodes on top of the insulating layer.

Thermally Insulating Encapsulation Material. Although commercial bismuth telluride modules used for Peltier cooling tend not to be encapsulated (working temperatures are typically less than 100 °C) TEG modules employ thermal insulation as the hot side working temperature can easily reach 200-300 °C. Oxidation of the thermoelectric materials and the solders is a possibility as well as the loss of TE material due to vaporisation, both of which can lead to the long term degradation of performance. Higher temperature modules require more extreme encapsulation methods such as ceramic fillers, aerogels or full metallic or ceramic encapsulation.

Joining Materials. The choice of joining material is dependent on the operating temperature of the module, with the maximum operating temperature typically 50-100 °C less than the melting point of the joining material. For operating temperatures less than 450 °C, lead-free solders are usually employed; for temperatures above 450 °C a braze is utilised. Copper and nickel electrodes typically employ a silver-based braze while aluminium electrodes require an aluminium-based braze. Joining materials need to be carefully chosen to avoid thermal stresses. To prevent the diffusion of material between the electrode and solder, barrier layer coatings are employed.

Electrical Contact Resistance. This is a key consideration when designing modules since it represents a loss mechanism that can reduce the output of modules. The contact resistance is usually multiplied by the cross-sectional area of the leg to give the specific contact resistance (SCR). The SCR is dependent on a number of factors such as the materials composition and operating temperature and the choice of bonding materials and barrier layers are important factors when considering long term performance of the module.

Thermal Contact Resistance. Thermal contact resistance can influence the performance of a thermoelectric module both in Seebeck and Peltier mode. Any significant gaps resulting in air pockets at the interface between the module and heat exchanger can dramatically reduce heat conduction. Surface polishing is one possible solution but this is expensive and time consuming. Alternatively, thermal transfer pastes can be employed; they can be easily applied and provide a close contact between the two surfaces. Pastes do have a limited operating temperature and may degrade with time. Consequently, the use of a graphite interface layer is increasingly preferred by module manufacturers.

3.2   Current Module Research

Low Temperature
Bulk (flexible). A team lead by Ozturk [22] have developed a novel concept based on the standard thermoelectric architecture but that is completely flexible. Bismuth telluride based legs are connected by

electrodes which are made of an indium-gallium eutectic which is liquid under ambient conditions. The legs and electrodes are encapsulated and held in place by an elastomer which allows complete flexibility and has been shown to have self-healing properties if an electrical connection becomes damaged. The intended use is for a non-intrusive power supply generating electrical power from body heat to supply medical devices. Currently the limitation on the device is the low power generated. This could be improved through improving the thermal conductivity of the elastomer.

Printed Thermoelectrics. Thanks to the advances in printing technology (2-D and 3-D) it is now possible to print thermoelectric modules accurately in a two stage process. The first stage is to take an ink which has the thermoelectric material in suspension and print onto the substrate. Subsequent layers can then be added to form the 3-D printed structure. The second stage is to sinter the thermoelectric material together to form a mechanically strong and electrically conducting material which maintains the thermoelectric properties. In principle it should also be possible to print the electrodes and the insulating layer which would simplify the manufacture of modules considerably.

Mid Temperature

There is a large volume of research and manufacture into devices that operate in the mid-temperature range by companies, research organisations and universities all over the world. Table 2 provides a selective highlight of the main material systems from which modules are being produced and gives examples of where they have been integrated into an applied test system. The Fraunhofer IPM (Germany), are currently taking materials developed in the lab and up-scaling to industrial-scale prototyping of thermoelectric modules. They are investigating two material systems, skutterudites and Half-Heuslers and have invested in large scale Spark Plasma Sintering (SPS) and Pick and Place technologies to produce 160 modules in a single test batch. This holistic approach supports the transition from materials development to full scale application testing and is supporting industry in the implementation of future technologies.

Table 2: Some example manufacturers and systems installed for various mid-temperature systems

Material system	Typical operating ranage/^{o}C	Selected module manufacturers and efficiencies	Selected systems installed and power output/W
Tetrahedrites-Magnesium silicide	200-600	Alphabet Energy 5%@ T=300 K [23]	Alphabet Energy claims a system produces 900 W of power from a hot gas temperature of 550 °C and flow rate of 9 m^3 min^{-1}
Skutterudites	300-600	NASA 8% @ T=400 K [24] Marlow7% @ T=460 K [25] Fraunhofer 7% @ T=430 K [26]	NASA eMMRTG system can produce 145 W. BMW have installed a 57 W system
Half Heuslers	300-700	Fraunhofer 5-6% @ T=530 K [27]	200 W generator tested by Evident Thermoelectrics
PbTe-TAGS	200-600	NASA 6% @ T =330 K [24]	NASA have installed a 110 W RTG system on two space missions. 300 W generator tested by BMW.

Segmented Modules. Segmented modules hold great promise for enhanced efficiency for a given temperature difference. Typical ZT for a given material peaks over a narrow temperature range with the average ZT over the temperature range being much lower. As discussed in Section 2.2 an increase in the average ZT over the temperature range of operation has a greater impact on efficiency than increases in the maximum ZT. It is possible to improve the average ZT by using a combination of thermoelectric materials joined together in the leg structure, thereby producing higher efficiencies. However, forming a segmented module is a complicated process with different materials having different thermal and mechanical properties. Without careful design, stress points could appear in the module under operating conditions. Although joints are typically the strongest part of a module, the region directly next to the joint is a potential failure point. The more joints present in a module, the greater the chance of a mechanical failure. NASA has led the way in developing segmented couples, with their skutterudite-Bi_2Te_3 systems, with an efficiency of 13.5% reported [28]. Lidong Chen's group in China has recently published an efficiency of 12% for a skutterudite:Bi_2Te_3 module [29]. The AIST group in Japan report an efficiency of 7.5% for a clathrate single crystal/Bi_2Te_3 segmented module with a power output of 0.87 W and a hot side temperature of 380 °C [30].

High Temperature. Si-Ge has long been established as the material system to use at high temperatures of 600 °C-1000 °C (and above) since its development for radioisotope thermoelectric generators (RTGs) in the Voyager space missions. Subsequently this system has been used in automotive waste heat recovery (Nissan, Japan) but was found to be limited in its usefulness due to the lower average operating temperatures of automotive engines [31]. Further enhancement in the ZT value at lower temperatures, or the use of segmentation, is required to make Si-Ge commercially viable.

Another contender for high temperature applications are the ceramic oxide material systems. Most of the research is still at the laboratory stage but commercial modules are now becoming available with reasonable power outputs but limited efficiencies. TECTEG MFR have a ceramic metal oxide TEG available which is capable of generating 12.3 W at a temperature difference of 750 K (hot side temperature 800 °C)[32].

4. THERMOELECTRIC APPLICATIONS

4.1 Automotive/Internal Combustion Applications/Challenges

The principal application areas for TE in the light duty (passenger car and light freight vehicles) are respectively HVAC (heating ventilation and air conditioning) and WHR (waste heat recovery) from engine systems, and in particular the engine exhaust flow. The relative simplicity of the TE architecture is a good match to the passenger [33] car application where increases in complexity and mass carry a high penalty.

HVAC systems may consume up to 3 kW of engine power to support the refrigeration pump and air circulation. Proposals for TE based systems will use devices to heat or cool the incoming air and to manage the temperature of surfaces close to the vehicle occupants.

Proposals for WHR visualise a heat exchanger in the exhaust gas flow with heat transfer to ambient air or engine coolant. Limitations include the very high temperatures that can occur under transient conditions, elevated back pressure applied to the engine and interference with the temperature distribution required for treatment of the exhaust gas.

In heavy duty and larger applications of engines (above 300 kW rated power output), TE technologies face a stiffer challenge. The lifetime fuel consumption of such engines usually exceeds twenty times their value which opens up a wider range of technology options that includes Rankine cycle and supplementary expansion of exhaust gases. However, the solid state and distributed nature of TE power supplies is attractive as a solution for wireless sensor networks in high value applications of engines such as marine, power generation and locomotives. Similarly, even with the anticipated reduction in the numbers of new petrol and diesel cars from 2040 there will still be significant opportunities for TE power in hybrid and related vehicles for several decades.

While the pressure for fuel economy varies as fuel costs vary, the need to meet the requirements of carbon dioxide emissions legislation currently provides the greatest pressure on the light-duty sector. TEGs are mentioned in both the EU2021 CO_2 regulations and the US EPA/NHTSA 2025 Fuel Economy/CO_2 regulations. In both cases they are referred to as 'off-cycle' credits, meaning potential additional credits which cannot be measured on the formal test cycles (credits here refer to the calculated reduction in fleet emissions). In both Europe and United States TE is only one of a series of possible measures that passenger car manufacturers can adopt to meet the new requirements.

Recent activity in the UK has included the Innovate UK funded VIPER and VIPER2 projects (Fig 9). See for example Brennan et al. [34] for comments on the challenges facing the design of heat exchangers. EU funded projects in which UK organisations have played a role include PowerDriver (2012-2014) and more recently, Integral (started 2017) and Ecochamps (2016-18). Experience from the VIPER project suggested that cost projections for a TEG based on Bi_2Te_3 were too high to make for a viable product.

Figure 9 (a) Image of VIPER2 thermoelectric module for vehicle application, (b) VIPER2 module fitted to underside of test vehicle. Both images courtesy of the Innovate UK funded VIPER2 programme.

While VIPER used bismuth telluride (Bi_2Te_3) and VIPER2 used metal silicide materials as the thermoelectric element, a consortium made up of Reading, Cardiff and Loughborough Universities (UKTEG) worked under EPSRC funding to develop skutterudite materials for the WHR application. The particular attraction of skutterudite materials is their ability to work at normal engine exhaust temperatures. The result of this work included n and p forms of material well matched to the exhaust temperatures of a small passenger car

engine [35]. Power output predictions over formal test cycles suggest average outputs of 300-500 W with a heat exchange architecture that still has the potential for significant improvement.

It is clear from the VIPER and UKTEG experience that new manufacturing techniques are needed to facilitate the kind of heat exchange architectures that will be cost effective through being well matched to the conditions of the engine exhaust. From recent work on catalyst systems reported in the United States [36] and earlier activity [37] in the explicit temperature management of catalyst systems there is a developing interest in the integration of the principal exhaust system functions that may include TE components.

Energy harvesting using waste heat from internal combustion engines (ICEs) would extend beyond the automotive sector if efficient materials containing abundant elements were to become available. Even with the 2017 announcement by UK Government [38] of the plan to end the sale of all new conventional petrol and diesel cars and vans by 2040, there will still be very large numbers of vehicles in the UK and overseas which are totally or partially reliant on ICEs well beyond 2040. A recent report from MIT [39] suggests that by 2050 between 60 and 90% of light and standard vehicles (depending on energy change scenario) will still use ICEs. Indeed there are many other ICE-based applications in transportation and other sectors. With marine transportation accounting for ca. 5% of global CO_2 emissions (over twice that of aviation), TE energy recovery in the marine sector would have a significant impact on the worldwide emissions total. The electrical power provided would augment or replace that from the on-board diesel-fuelled generator sets (0.5-1.5 MW output) that are commonly used to provide on-board electrical power and which add significantly to a vessel's fuel consumption. Early trials at the Maine Maritime Academy [40] using current generation commercial (Bi_2Te_3) TE modules have demonstrated that TE power generation holds considerable promise for the maritime industry but that new high efficiency materials are required to achieve economic viability.

4.2 Wireless Sensing

Wireless Sensing Networks (WSN) are of increasing interest and importance for condition monitoring and control in a wide variety of environments from industrial to domestic. The sensing could include: wearables for medical diagnostics; sensors in domestic settings to control appliances or the building environment, wearables in sport in order to provide real-time performance data, industrial plants for remote monitoring of gas flows, temperatures, pressures needed for process control, aerospace, monitoring of key functions in jet engines. Different types of WSN have been in use for many years but the rapid expansion of connectivity has led to the Internet of things (IoT), or the inter-networking of physical devices, providing network connectivity which will enable these objects to collect and exchange data. There are estimates that the IoT will consist of about 50 billion objects by 2020 [41]. This will provide increasing opportunities for thermoelectric powered systems.

WSN have very modest power requirements in the µW – mW region. Some of the existing TE harvesting power systems can operate with temperature differences as low as 2 °C. [42]. For such TEGs, only small quantities of material would be required, making it an application area suitable for thin and thick film TEs perhaps, which would make integration with the electronic devices more straightforward.

The UK already has plenty of IoT and WSN activity in protocols and systems, but expanded activity in powering WSNs and the IoT would benefit the UK economy.

4.3 Aerospace

In the aerospace sector, radioisotope TEGs have been used by NASA for over 50 years for a variety of missions and craft; latterly these have included the Mars Rover, Curiosity, the Galileo satellites, New Horizons space probes, and Cassini spacecraft [43]. Commercial and military aircraft already use sensors and sensor networks powered by thermoelectric generators to monitor the aircraft skin for damage that can cause stresses and structural weakness [43]. In one example a traditional bismuth telluride TEG generated about 20 to 30 mW of power from the heat of normally operating turbine engine bearings, which was more than enough to power the network of embedded sensors [43].

TE devices are also used in the following applications in the aerospace sector for: Avionics cooling (in a number of types of equipment); Black Box Coolers; Drinking Water Coolers; Space Vehicle Refrigerator/Freezers; Temperature Control for Space Telescopes/Cameras. Size and weight considerations are paramount in the aerospace industry and performance per unit weight is the key parameter. The current low efficiencies may impose a constraint on applications such as cabin air-conditioning where large amounts of cooling are required.

New areas of application that would be opened up to new high-efficiency devices would include energy recovery from waste heat from jet engines on aircraft. Effective use of waste heat is currently a hot topic in the aviation industry. Initially, restricting TEGs generators to the provision of power for non-safety-critical functions, such as in-flight entertainment systems, would obviate many of the barriers to implementation in a heavy safety-regulated industry. Indeed BAE Systems Military Aircraft and Information (MAI) at Warton are already considering potential applications for Thermoelectrics on future combat aircraft projects which include: (i) Future aircrew clothing - multiple applications of integral novel materials / devices within fabric, including thermoelectric; (ii) Supplementary Electrical power generation from propulsion jet pipe, using thermoelectric; (iii) Incorporation of Thermoelectrics within certain Heat Exchangers to enhance system performance.

4.4 Wearable/implantable thermoelectrics

4.4.1 Level of Performance Required
For commercial applications, conversion efficiency is not necessarily as important as cost and power output. Ultimately, any solution will need to be able to power or at least charge devices in a way that surpasses current/future battery technology, either in terms of cost or convenience of recharging/replacing. To use TEG's alone to power wearables at room temperature is big challenge and would require new safe materials that are cheaper to produce at scale and can achieve much higher ZTs than have been demonstrated before. Below are examples of some of the most promising emerging materials for wearable thermoelectrics.

Electronically Conducting Polymers:
There are many electronically conducting polymers, for example, polypyrrole (PPY), polyaniline (PANI), polythiophene (PTH), poly (3,4-ethylene dioxythiophene) (PEDOT), polyacetylene (PA), and their derivatives. However, poly (2,7-carbazole), PEDOT, and PEDOT: polystyrenesulfonate (PEDOT:PSS) are good candidates for thermoelectric applications due to their process ability, high electronic conductivity and low thermal

conductivity, low cost, tenability in various sizes and shapes, and environmentally-friendly nature. In general, the figures of merit (ZT) reported for these materials so far are not high enough for high efficiency conversion of heat to electricity. Hence it is imperative to improve the figure of merit values further by using latest technologies and different approaches.

Carbon Nanomaterials:

The main drawback of using carbon materials for thermoelectric application is their high thermal conductivity. However, the thermal conductivity could be altered by nanostructuring materials. For instance, nanowires do not conduct heat due to phonon-boundary scattering or phonon dispersions. Carbon nanotubes, carbon nanowires and graphene are potential candidates for TE materials due their good electrical conductivity and the thermal conductivity could be adjusted. In addition, high mechanical strength and high thermal stability are advantages for flexible TE devices.

Carbon Nanotubes:

CNTs are one-dimensional carbon nanomaterials with diameters and thicknesses in the nanoscale region. n- and p-type CNTs can be fabricated, which is beneficial for manufacturing TE prototypes. Doping results in a decrease of thermal conductivity by up to 75 % as a result of the defects induced inside the multiwall carbon nanotubes (MWCNTs). By oxygen doping it should be possible to increase the density of charge carriers, and thereby the Seebeck coefficient. A five cell p- and n-type MWCNTs thermoelectric module could produce a thermoelectric power of 16 μW at 27 ^{o}C [44].

Graphene:

Although the zero bandgap of graphene results in a very low Seebeck coefficient and a very high thermal conductivity, theoretical investigations indicate the potential of graphene for thermoelectric applications. For instance, studies on zigzag graphene nanoribbons show that a ZT of 4 could be obtained at room temperature, providing the significantly reduced lattice thermal conductivity could be induced via phonon-edge disorder scattering, while the electron transport is maintained [45]. Graphene possesses very high electrical conductivity, with a very high electron mobility of 1000-7000 cm^2 V s^{-1} [46]. Wei et al. reported a thermopower of 50-100 μV K^{-1} at room temperature for a graphene sample exfoliated onto a thin layer of SiO$_2$ [47] It should be noted that hybrid nanostructuring can decrease the thermal conductivity of graphene by up to 98.8 % at room temperature. Therefore, graphene nanoribbons fabricated with atomic precision could improve the thermoelectric performance [48].

4.4.2 Intermediate steps that would open up new opportunities

In general, there are four main designs of TE modules for wearables: single stage, multi stage, hole type and micro type TE modules [49]. The dimensions of single stage TE module are around (10 – 30) x (10 – 30) mm while that of multi stage TE module are around (10 – 50) x (10 – 62) mm. Although the multi stage TE module is not perfect for wearable TE generators in term of flexibility, weight, comfort, it is still the most popular design for high power generation. The dimensions of a hole type TE module are around 4.7 -10 x 25 mm (round hole) and 8 x 22 mm (square hole) whilst that of micro type TE module are around 2.2 x 6.3 mm. The Smart thermoelectrics company manufactures a 3-stage "ME Series" TE cooler which provides higher conversion efficiency than those of single stage modules [49].

For a staged commercialisation of wearable TEG, a series of steps beginning with commercially-available Bi$_2$Te$_3$ based TEG technology at room temperature, and then a multi stage TEG design would be the best

route for improving the energy conversion efficiency. As advanced materials, derived from polymeric and carbonaceous materials, optimised for the operating temperatures become available, they would begin to replace Bi_2Te_3 in wearable devices. A multi stage design would be a stand-alone device rather than being integrated into the textiles. While this would not represent the best solution, it would demonstrate the proof of principle and begin to raise awareness of the technology with the general public. The example of an Indiegogo campaign demonstrates that TEG for wearables could be quite successful. The campaign raised $1.4 million to deliver a TEG powered smart watch, purely through public crowd funding [50].

The next step would be to embed TE generators into textiles and develop solution processing TE technology such as textile coating and ink-printing. Thus, nanostructuring, solution or organic based TE generators are of interest. Lu et al. [52] reported a process of nanostructured Bi_2Te_3 and Sb_2Te_3 deposited on silk fabric to fabricate columns of n- and p-types of TE generator. This technology has potential for commercially wearable TE generators if it can be made at scale.

4.4.3 Technical Constraints and Principal Markets for Wearable Thermoelectrics

The structural complexity [53], difficulties in fabrication of high-quality materials [54], low energy conversion efficiency and fabrication cost [55] are currently the biggest limitations for wearable thermoelectrics.

For wearable TEGs integrated into e-textiles that incorporate conductive fibres in the textile itself, e-textile TEGs, certain criteria need to be met. Any future solution would need to be:

- Flexible while possessing a high mechanical strength
- Comfortable, environmentally friendly.
- Highly compatible, lightweight, modifiable.
- Easily embedded into human clothing while allowing them to retain enough of the clothing's desirable physical qualities (i.e. stretchable, foldable, washable, breathable, comfortable)
- Made from abundant raw materials, in order to keep material costs down.

Sporting and military would be the most appropriate markets due to the higher temperature differences generated through physical activity. For the military, the principal application of wearable thermoelectrics is likely to be the cooling of personal protection suits and environmental control within armoured vehicles. An increase in military activities in hot climates increases the need for a better solution. A significant improvement in ZT performance would expand the potential of this market enormously.

Inside the human body the average heat flow is 58.2 W per square meter due to the basal metabolic rate; this could be as high as 100 W per square meter during physical activity. However, the human body has a high thermal resistance at ambient temperatures below 20-25 $^{\circ}$C [56] which reduces heat flow. Depending on the location on the body, heat flow can be anywhere between 1 to 10 mW cm^{-2} for typical indoor conditions. There will also be a difference between heat flow from a naked skin surface and through a textile garment. Clothing will ultimately affect the way heat will flow from the body to the surroundings and this must be considered during the design phase. As such, comparatively little heat is dissipated from the skin due to the thermal insulation of clothes (typically $3 - 6$ mW cm^{-2}).

The largest area of the body with the most stable temperature at different ambient conditions (temperature, wind, sunlight, etc.) is the trunk. However, this also presents the hardest task for adaption and implementation into e-textiles due to the criteria mentioned above. The skin temperature is still around 20 – 25 °C on the scale of centimetres. Therefore, the heat flow of a TEG embedded device would depend not only on the skin temperature, but also on the local thermal resistance of the human body (i.e, the thermal resistance between the body core and the chosen location on the skin).

Mechanical design is as important as device design because it affects not only the relationship between the thermal transportation and the contact but also the performance of a device. It must be comfortable, allowing high mobility, and also be flexible and biocompatible. Mechanically flexible devices can be achieved by direct fabrication on plastic foil, or by peeling off a polymer layer deposited on a rigid substrate by ink-printing [57].

The criteria for a system integrated into a piece of clothing is that it must be thin, lightweight, waterproof, bendable and sustain repeated laundry and pressing or high temperatures. High accelerations and mechanical shocks during machine washing should also be considered; protection may be required. However, implementing protection methods might adversely affect the power output and partially decrease the convective and radiation heat transfer from the TEG.

4.5   Building Scale Integration

4.5.1 Thermoelectric Wireless Sensor Networks

In recent years there has been growing interest in the construction of sustainable high performance buildings where the ambient building environment can be controlled in a dynamic way. The traditional methods of controlling temperature, humidity, air quality and artificial lighting etc, are through the installation of distributed wireless sensor networks (WSNs). These can result in energy savings of approximately 20% and a major step towards real Smart Building Management [58]. Unfortunately, traditional WSN rely on battery powered sensor systems, with inherent disadvantages of the need for regular and long term maintenance. Such limitations could be overcome by WSN systems powered by stand-alone, micro-scale thermoelectric generators, which obtain their power by energy harvesting. Millimeter scale TEGs such as those produced by Micropelt [51] are reported to be able to generate 200 μW of electrical power from a temperature difference of 3.5 ^{o}C which is sufficient to broadcast data once per second in a wireless sensor node [59]. Huang et al [58] reported a very effective TEG powered building WSN demonstrator which worked with temperature differences of 3–8 ^{o}C. Later Kuchle and Love [60] employed thermoelectric sensing loops and realised a WSN system which could monitor directly temperature and magnetic field strength via an integrated Hall monitor.

4.5.2 Transpired Solar Collector Systems

Other opportunities for building scale integration of thermoelectric devices include solar thermal collection by Transpired Solar Collector (TSC) in industrial buildings [61]. This is an established technology that can produce significant savings in heating costs (Table 3). Thermoelectric devices can be integrated into products, such as Tata Steel's Colorcoat Renew SC [62], or Conserve Engineering's Solar Wall [63] to enable building-scale generation of power from the heat generated by near-infra red; absorbent coatings can heat surfaces to ~ 70-90 ^{o}C [64], giving a temperature gradient of ~ 50-70 ^{o}C compared to the ambient indoor

temperature. The efficiency of these systems could be increased by combining with thermoelectric generators to power the electrical systems (fans, vents, etc), of the TSC system.

Table 3: Commercial installations of Transpired solar collectors for ventilation air heating [61]

Project	Location	TSC area m^2	Predicted Energy Savings kWh/yr
Jaguar/Land Rover	Leamington Spa	268	80 530
Beaconsfield Services	Beaconsfield	255	99 235
Premier Park	Winsford, Cheshire	580	130 000
Sainsbury's Distribution	Pineham	947	256 093
CA Group Rollforming Mill	Evenwood	1211	299 000
International Paints	Felling, Gateshead	100	31 169
Royal Mail	Swan Valley	800	233 396

4.6   Application of TE in General Industry and Power Generation

The most successful and widely reported applications of TE have tended to be in "high value" environments. With cost reduction and improved engineering, TEGs suitable for general industrial use are emerging for application in metals and glass manufacturing. Processes are characterised by high temperature gas flows that flow through ducts and chimneys, facilitating the deployment of TEG systems.

The United States Department of Energy (DoE) in its 2015 Quadrennial Review of Technology [65], highlights the energy sectors where there is substantial potential for "retrofit" energy recovery systems. Case studies illustrate the benefits. Alphabet Energy offered a TE based WHR system for diesel generator sets able to recover 25 kW from the exhaust stream of a 1MW rated engine. A review of a steel mini-mill in Jewett, Texas demonstrated substantial energy recovery from hot steel slabs during the rolling process.

While the direct application of TEGs to industrial processes offers substantial opportunities for energy recovery, there are also niche applications where the strategic deployment of a high temperature TE system can offer significant thermodynamic advantages that may lead to the simplification of the plant [66].

4.7   Nuclear Industry

Nuclear fission reactors produce considerable quantities of heat to create steam that drives the mechanical turbines, which generate electrical power. However, there are inherent limitations in the efficiency. For example a typical reactor producing 1000 MW (thermal) operates at 25-30% efficiency as a result of constraints imposed by the Carnot cycle and the limitations of steam turbines. Such plants produce a steady supply of low-grade waste heat.

Extraction of energy from this waste heat would not only improve the overall operating efficiency of a plant, thereby reducing fuel consumption but also lessen environmental problems associated with the release of very hot water into neighbouring water courses. It has been proposed that a static energy recovery system, incorporating a TE converter operating at the bottom cycle (525 to 365 K) would markedly increase the total utilization of a reactor's thermal energy in a small gas-cooled reactor.

4.8   Geothermal Applications

Decommissioned offshore oil platforms have been suggested as a source of geothermal heat. Temperatures at the depth of a worked-out reservoir are 80-100 ^{o}C higher than at the surface. It has been estimated that up to 10 MW may be generated by exploiting the temperature difference between seawater at the surface and that which has replaced oil in the subterranean reservoir. However, with current thermoelectric conversion efficiencies, the economics of power transmission to the mainland are not favourable.

5.   THERMOELECTRIC ENERGY HARVESTERS: MARKET FORECASTS

The global market for thermoelectric generators in 2017 is estimated [67] to be US$ 320 million and is projected to grow to US$ 720 million with a growth rate of 14.5% from 2015 to 2021. North America is expected to dominate with over two thirds of the market, and to retain supremacy over the period. However, Asia Pacific and European countries are projected to grow at relatively higher rates. Beyond 2021 continued growth is expected with the market for thermoelectric energy harvesters reaching $875 million by 2023 [68], and $1000 million by 2024 [69], with thermoelectrics ahead of piezoelectrics in terms of investment and commercialisation.

The thermoelectric generator market is divided into four main segments, namely waste heat recovery, energy harvesting, direct power generation, and co-generation.

In 2015, waste heat recovery was the largest segment of the thermoelectric generator market. In spite of policy changes in the UK [38] and elsewhere about planned reductions in sales of new petrol and diesel cars, a significant fraction of the automobiles on the road will still contain internal combustion engines [39].

The automotive sector was one of the key applications areas in 2015 and is expected to remain an important market.

Aerospace and industrial heat applications are in second and third positions. The industrial segment is expected to see considerable growth in the next few years due to the availability of low-cost devices.

Another area that is expected to grow significantly in the coming decade is the low power, sub-watt TEG market, with predicted compound annual growth rate of more than 110% from 2014 to 2020 (Fig 10). These low power TEGs are focussed on two main applications area: infrastructure and buildings, and industrial and professional. Along with the emerging thin film/thick film devices they should be well suited to the expanding WSN and IoT markets.
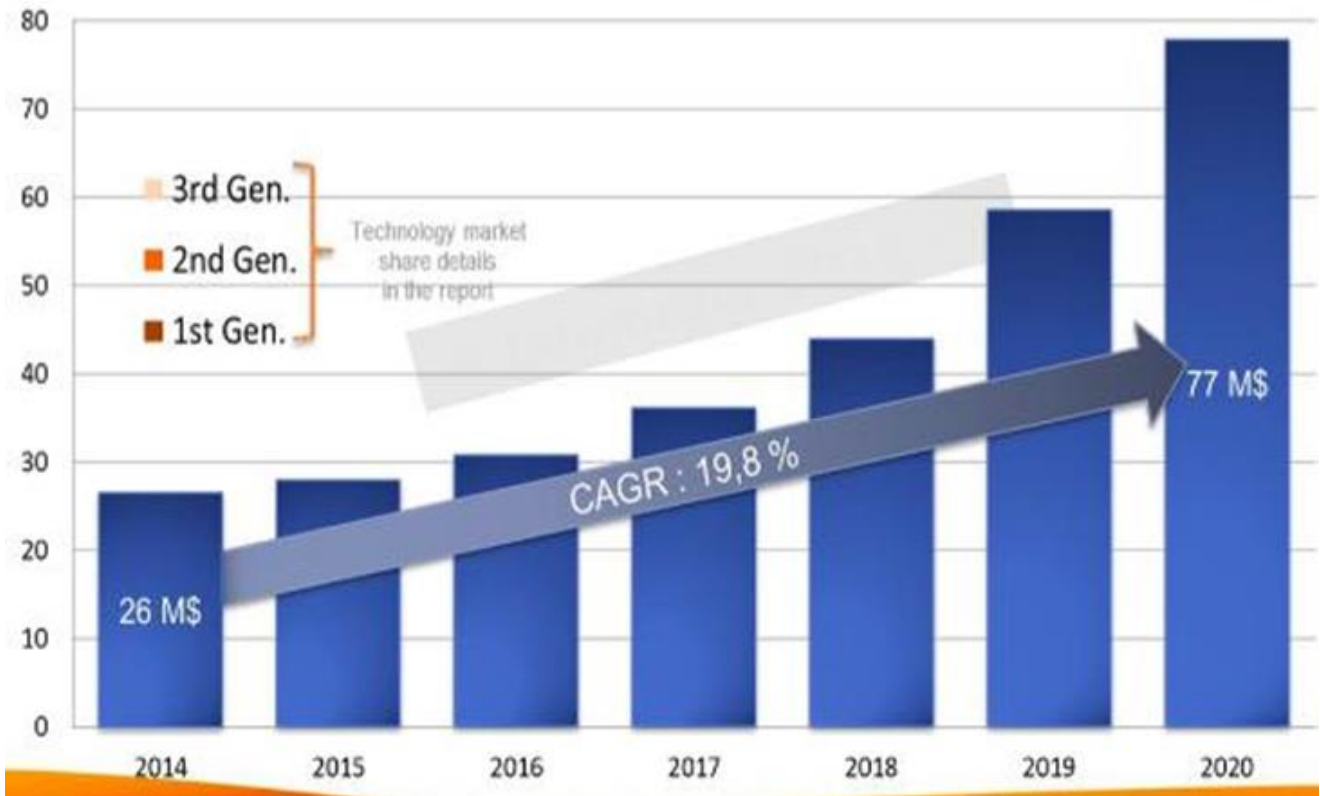
Figure 10: Market for sub-watt generators [70]

6. OPPORTUNITIES AND FUTURE NEEDS

6.1 Introduction

Solid-state heat management for energy harvesting and cooling are global business opportunities. The current global market for TE devices is approximately $300M and is predicted to grow to over $1Bn by 2024 (section 5) if the technical challenges associated with performance, cost and materials availability can be overcome. Therefore, business opportunities exist in the supply of TEG systems to a wide range of industries including manufacturing, nuclear, defence, geothermal, solar and sensors. The UK has in-depth academic expertise [71] and some associated businesses including TEG module manufacture and supply of thermal interface materials. The challenge now is to capitalise on recent advances in TEG materials from the academic community and develop practical system-level demonstrations that will greatly facilitate the uptake of the technology across business sectors. Examples of the opportunities for TE Harvesting & Cooling across a range of industry sectors are given in Appendix A. The market will be driven by: Environmental protection, Replacement of CFCs, Use of Waste Heat, Improvement in use of Energy, Global Warming.

With no change in ZT performance, the market should grow by about 15% per annum. Reliability of the finished device is of key importance in all sectors. Manufacturability and yield are critical. Material processing and module production technologies are often proprietary. It may be difficult to convince suppliers to invest in any modifications to these that are needed, in order to use the new material. For

cooling applications, compressor-based technology is very dominant and will take time to displace, even with better performance thermoelectric technology.

6.2 Materials

6.2.1 Bulk Thermoelectrics

There exist today a very wide range of bulk materials (Section 4) from the traditional and very well established metallic tellurides, skutterudites and half heuslers, to the sulphides, oxides, organic materials and composites. Whilst integration of the individual thermoelectric elements in TEG packages without degrading performance sets manufacturing challenges there are also fundamental materials challenges. Whilst peak ZT is still an important criterion for thermoelectrics and there are established strategies to increase electrical conductivity and reduce thermal conductivity in order to increase ZT, the importance of achieving a high average ZT over the temperature profile of the device is also becoming increasingly recognised. In recent years a number of novel approaches to improving materials' performance have emerged (Section 2.4.2). More theoretical and experimental investigations are required to better understand the materials at the nanoscale and to develop strategies to design material nanostructures that will lead to significantly improved ZT performance.

All of the known thermoelectric materials have well defined temperature ranges, or windows, where the material performs at near maximum thermoelectric conversion efficiency. In some cases the peak temperature windows are at very modest temperatures whilst for others it occurs at much higher temperatures, requiring the use of tandem modules to maximise thermoelectric power conversion from large temperature gradients. Specific challenges for bulk materials are to increase the overall ZT of the material, without degrading thermal or mechanical stability, but also to increase the width of the thermal window for thermoelectric power conversion. For applications involving transport any weight increase should be avoided, thus lightweight materials based on earth abundant, cheap elements are preferred.

6.2.2 Thin Film Thermoelectrics

As a direct consequence of module size, thin film generators are not appropriate for large-scale energy generation or recovery. However, thin film, energy harvesting TE micro-generators are ideally suited for smart, possibly flexible, "internet of things" applications including remote sensing and medical applications related to body heat harvesting.

One key issue related to the development of thermoelectric materials, particularly thin film thermoelectrics, is the scarcity of reliable reproducible data. A round robin sample exchange and calibration effort within the U.K. thin-film community would be very valuable both to establish and validate the performance data and the reasons for differences in the data. Indeed this applies to many other types of TE materials.

6.2.3 Organic Thermoelectrics

n-type OTEs: The development of doped n-type semiconductors is lagging behind p-type; the main reason being the high electron affinities (-3 to -4 eV) of many n-type semiconductors, making doping under ambient conditions difficult due to enhanced reactivity. To advance, the development of organic thermoelectric materials, novel air-stable dopants for n-type semiconductors need to be developed.

Self-powered sensors: Organic semiconductors are in general very sensitive to their environment, and exploiting this in combination with their thermoelectric properties has great potential for self-powered sensors. i.e. devices where the power source is also the sensing element. Self-powered dual pressure-temperature sensors have been demonstrated [14], but the possibilities could be expanded to sensors of humidity, salts, biological markers, and toxins amongst others.

Cost in OTE: In OTEG development, module cost per Watt ($/W) is best addressed by increasing ZT [17]. Currently models of thermoelectricity for organic materials are borrowed from the inorganic community. However charge transport in organic materials occurs by different and quite complex routes and is not universally understood. Equally the origin of the Seebeck coefficient in organics is not resolved, and methods to minimise thermal conductivity have not been extensively explored. Computational and experimental research on these key questions is still much needed. Nonetheless for organic materials (including n-types) it can be appropriate to pursue synthesis cost reduction approaches to expand the possible range of applications. The cost of substrates, heat exchangers and manufacture are as important as synthesis costs.

Doping strategies: Doping in OTEs generally comes from blending with molecular dopants. Unfavourable morphologies and dopant phase separation are commonly observed which limit the carrier concentrations in many OTEs. Strategies to maximise the degree of doping in these materials are needed. These are likely to be by chemical design (of semiconductors and dopants) and ink formulation. Chemical design strategies to doping would include control of miscibility of semiconductor and dopant, as well as new self-doped materials and intrinsically conducting polymers.

Molecular design: Most OTE materials are borrowed from the organic electronics field. There has been relatively little effort to design bespoke materials for the application due to a lack of design rules. Development of OTE material design rules by computation and experiment are a priority.

Printing and processing: Technologies for printing sub-micron organic electronic materials are well developed, but there will need to be significant adaptation to OTE which requires printing of thick films (10s-100s μm). Thus far, thick film printing has yielded reduced electrical conductivities, particularly in the out-of-plane orientation which is the usual direction of current flow in an OTEG. Similar challenges are faced for blade coating, extrusion, melt processing etc. These challenges may be addressed by new ink formulations, process control and by redesigning device geometry.

Composite materials: Organic materials can be readily processed into composites by a range of scalable techniques. A new range of composite materials aimed at OTE applications will open up many possibilities. These could be composites to boost electrical conductivity by combining the OTE with a more conductive material; or composites to bring additional functionality such as enhanced flexibility, stretchability, ion sensing, and pressure sensitivity amongst others.

6.2.4 Flexible Thermoelectrics

Flexible materials, which are likely to be organic or composite in nature offer many possibilities in the wearable and medical sectors. The wearables already include clothing for sport and military personnel (section 4.4) and there are growing opportunities for clothing for aircrew, where integrating novel materials/devices (including thermoelectrics) within the fabric will enable control temperature within the suits. For medical applications temperature differences of 2 °C over an area 4 cm^2 should be sufficient to

power ultra-low power medical monitors for temperature, flow rates, ECG, EEG etc. Low thermal conductivity may be more important than high ZT for wearable medical applications. More general challenges that require more work are joining of new composite materials in TE modules, development of protective coatings and mechanical durability.

6.2.5 Modelling of Thermoelectrics

The UK has long had a strong tradition in materials modelling at the atomic level, which encompasses both the treatment of electronic properties, including reactivity, of typically 10-100s of atoms to molecular modelling where the dynamics of millions of atoms can be simulated. The community is helped both by strong supported networks, which also ensure that software is maintained and developed, such as through the CCPs (Collaborative Computational Projects), e.g. CCP5 and CCP9, and also through the increasing rise in high-performance computing, which allows for complex problems to be addressed. These developments allow materials modelling to underpin experimental research for the search and characterisation of new thermoelectric materials. For example, there is increasing use of high throughput computational screening to identify target structures and compositions that not only allow the stability of the phase to be verified but also whether the figure of merit, ZT is of a sufficient value to be worthy of further consideration. Indeed, in the US, the Material Genome Initiative [72] has been particularly effective in supporting high throughput computational materials design.

Modelling can also underpin and rationalize the different components of the structure and their contribution to the TE figure of merit, which is currently unattainable experimentally. This includes the search for dopants and microstructures, particularly nanostructures, to lower the thermal conductivity, while increasing Seebeck and electronic conductivity through band engineering.

Our fundamental understanding of carrier transport inside bulk materials has improved significantly in the last decade, mostly as a result of the use of first-principles approaches combined with high-performance computing. However, some key challenges will need to be addressed in order to take a step forward towards the design of complex nanostructured materials for the next-generation of thermoelectric devices.

For example, the electronic band structure of thermoelectric materials is routinely calculated from first-principles, usually using density functional theory (DFT). However, in semiconductors and insulators, DFT systematically underestimates the band gap by 30–40%. This is problematic especially for narrow gap thermoelectric materials, in which bipolar effects are important and accurate band gaps are required. For instance, the Seebeck coefficient is very sensitive to the relative position of the conduction and valence bands (band-gap) and to the band curvature near the gap edges. The accurate description of these features goes beyond the standard DFT. New numerical approaches have recently been proposed to overcome these issues, offering new avenues to be explored in the near future.

Another big challenge is the development of accurate and efficient computational tools to predict electrical transport coefficients. The main issue here is a proper description of the dynamics of carriers, while accounting for the relevant carriers' scattering mechanisms. In this context, the Boltzmann transport equation (BE) offers a framework for a detailed microscopic description of transport in metals and semiconductors. In order to achieve the full predictive power of this theory, further efforts are needed towards the exact solution of the BE, also accounting for accurate materials' parameters (electronic band structures and electron-phonon and electron-defect scattering terms) computed from first principles. This is

a computationally challenging problem, which will require in the future further optimizations to describe materials of interests for thermoelectric applications

Finally, further advances are needed to understand and predict carrier (electrons or phonons) transport in the presence of interfaces. Indeed, for instance, boundaries can have a significant effect on the overall thermal resistance as the interface density increases in nanostructured composite materials. As the structure of interfaces varies significantly from one grain to the other, the actual microscopic details of an interface are usually unknown, and this makes it very hard to compare theory with experiment. First-principles approaches can be used to model perfect interfaces at low temperatures, but it is very challenging to reliably predict trends for the thermal interfacial resistance change in the presence of defects, roughness, dangling bonds, and also accounting for anharmonicity and electron-phonon coupling. Future efforts are needed to overcome these limitations, by using other numerical methods based on molecular dynamics or the Green's function approach.

6.3   Thermoelectric Generators and Systems

6.3.1 Modules

The main focus of thermoelectric research is rightly placed on materials development to improve thermoelectric module performance. There are a few areas of device research which can complement this research and help advance the technology:

(i) <u>Batch reproducibility.</u> A dedicated research centre where promising materials developed by researchers on the small scale can be manufactured on the larger scale to test the scaled-up performance would be very valuable. This may also include accelerated life-time testing such as thermal/mechanical ageing targeted for their specific application.

(ii) <u>Module system efficiency.</u> Most TEG systems require more than one module and further work on understanding how modules interact with each other and maximise their overall performance is important for minimising the drop from module efficiency to system efficiency.

(iii) <u>Thermal interface materials.</u> Currently for high temperature applications graphite is the material used. Could it be possible to grow thermal interface materials on the module substrate or develop a process which will smooth the surface of the module without the need for polish?

(iv) <u>Joining material research.</u> There are very few solders/brazes which operate between 300 - 500 °C. The currently-available silver brazes have melting points above 600 °C and are expensive.

(v) <u>Segmented module systems.</u> There can be large efficiency gains from using multiple materials each with peak ZT values at different temperatures, in a single thermoelectric leg, in order to raise the average ZT.

6.3.2 Electronics for thermoelectric power generation

The principle of using a DC --> DC power converter to produce a constant output voltage from the temperature-dependent voltage from a thermoelectric generator (TEG) is well established. In many cases the desire is to maximise the total amount of energy extracted from the TEG material, and to do this the

input impedance of the converter is adjusted to match the internal impedance of the TEG at any given instant in accordance with the requirements of the Maximum Power Transfer Theorem. A particular challenge for low voltage electronic converters is to establish the first switching event (the so-called "sub threshold problem") and a number of integrated devices are starting to appear which control a resonant converter topology able to start from less than 100 mV. Once switching operation is established, operation down to as little as 25 mV from the TEG is quite practicable. However, sub-threshold converters are an active and growing research topic and will continue to be for many years.

From a systems perspective it is essential that the electronic converter is considered as part of the overall thermoelectric design from the outset. Areas that require particular attention are:

(i) Establishing the Maximum Power Point. The maximum power transfer theorem dictates the required converter impedance at the module level. However, at the system level where there are thermal gradients across the heat exchangers as well as the module, then by reducing the current flowing in the module, the heat flux decreases (due to a reduced Peltier effect) and this in turn reduces the temperature gradients on the heat exchangers, leading to higher available power from the thermoelectric material. In general this deviation from the predictions of the maximum power transfer theorem has to be empirically determined over the operating range of the TEG system which requires new control algorithms for the electronic control.

(ii) The voltage/current compromise. Many of the "new" TE materials such as silicides and skutterudites have a low electrical resistance which leads to a low output voltage and high output current. From an electronics perspective, losses increase as the square of the current flowing, and hence high current systems have an inherent disadvantage in terms of the maximum efficiency attainable. A secondary consideration is the cross-sectional area and hence mass (and cost) of the conductors between the TEG material and the converter(s) - for "mobile" applications such as automotive and aerospace systems the mass in particular is critical and if the voltage from the TEG array is too low the weight limits for the design are unlikely to be met.

(iii) Conversion and tracking efficiency. There are two figures of merit for the TEG converter: the accuracy with which it can track the real maximum power point (target >99%) and the intrinsic converter efficiency (target > 97%). The former is largely determined by the control algorithm. New algorithms are required for efficient transient performance and to be able to maximise system power output. A tracking algorithm that incorporates measurement of the delta T on a TEG module has been demonstrated to produce 7% more power than predicted by the maximum power transfer system alone. Much work is needed to convert this class of algorithms from "system specific" to "generic".

(iv) High temperature electronics. In order to reduce the mass of the electrical interconnection between the TEG and the converter, the converter is being moved closer to the TEG array which leads to a higher operating temperature, pushing the performance of available electronics to the limit. An emerging area exploiting TEG technology is down-hole "smart" drilling where the ambient temperature can easily exceed 200°C. New electronic devices are required to maintain the desired conversion efficiency under such conditions - not just transistors such as SiC and GaN, but circuit board materials, microprocessors etc.

6.3.3 Technological & Manufacturing Opportunities

Already, earth-abundant materials have been demonstrated in laboratory studies to be suitable for replacing expensive bismuth telluride in certain TEG applications. The next generation of materials are incorporating advances in nanotechnology including nano-structuring, 2-D layered materials (graphene and graphene-like)

that promise to show performance improvements beyond bismuth telluride. It is noted that more efficient materials need to be developed with an emphasis on maximising the average value of the figure of merit (ZT) rather than the maximum value, and optimising ZT for the application.

When coupled with advances in the other system components such as heat exchangers and thermal interface materials, TEG solutions to waste-heat recovery or cooling will be better able to offer alternatives to existing technologies as well as create new markets. The current generation TEG has multiple components – thermoelements, barrier/diffusion layers. solders/brazes, contacts, electrically insulating ceramics, all of which need to be assembled by (currently) hand. This is labour-intensive and therefore costly. Thus scale-up know-how is a key objective in order to reduce cost, which in turn will open up a wider range of applications. There is potential to exploit innovative manufacturing including 3-D printing, reel-to-reel and more robotic processing with existing materials. This should also enable the development of conformal, customised systems that enable much improved thermal interface-matching. Thus, there is plenty of room for the TEG industry to benefit more from economies of scale and novel processing methods including multi-kilogram semiconductor powder preparation to fast-throughput powder-sintering operations. We note that the environments and power ranges for waste-heat conversion to electrical power are particularly diverse, i.e. from jet engines to body sensors, and so require correspondingly diverse TEG materials.

Design and fabrication of new device architectures and provision of materials that enable novel architectures are required. One approach to improve the automation/production of TEGs would be to use processes such as printing, additive layer manufacturing, and adaptation of semiconductor industry processing tools. Heat transfer at interfaces and heat exchangers are an important aspect of integrated design. Increased understanding through modelling of what happens at interfaces is likely to be needed. Flexible or conformal module formats will help more efficient heat transfer from the source to the hot/ cold sink. One approach to meet this challenge is being met by the availability of novel organic and hybrid TEG electrode compositions as well as inorganic ones, which in-turn require innovations in their large-scale manufacture and system packaging.

6.4   Applications Sectors

6.4.1 Transport - Automotive
Power range opportunities: a few hundred Watts to a kilowatt
Power-train development for transport is undergoing significant changes with the progressive entry of hybrid and full electric vehicles into commercial fleets. For the conventional internal combustion engine, legislative drivers are forcing manufacturers to look for new ways of improving fuel economy such as the use of TEGs for utilising waste heat. In 2015 the UK used 57 million tons oil equivalent for all forms of transport (mainly road) with an associated CO_2 release of ~167×10^6 metric tonnes. Even modest waste-heat conversion with a 10% efficient TEG is calculated to decrease the net UK CO_2 transport sector emissions by several million tons. In addition, better management of passenger/driver comfort through selective cooling (or heating) could open up new TEG applications within the vehicle. Figure 11 shows a Technology Road Map for TEG and Peltier modules for automotive applications.
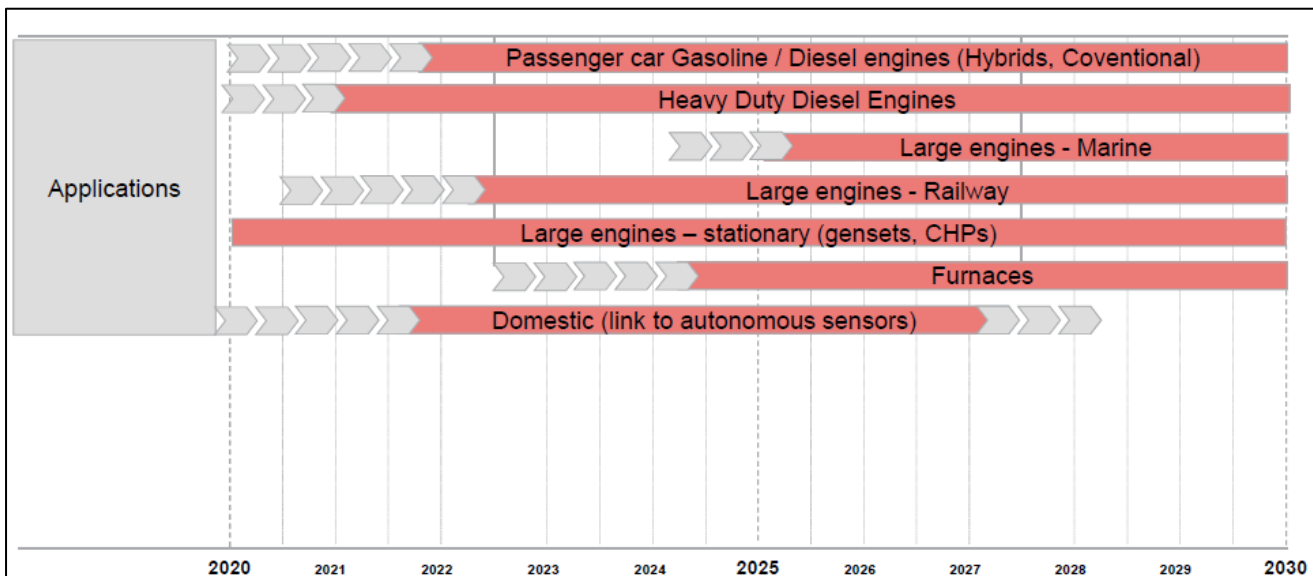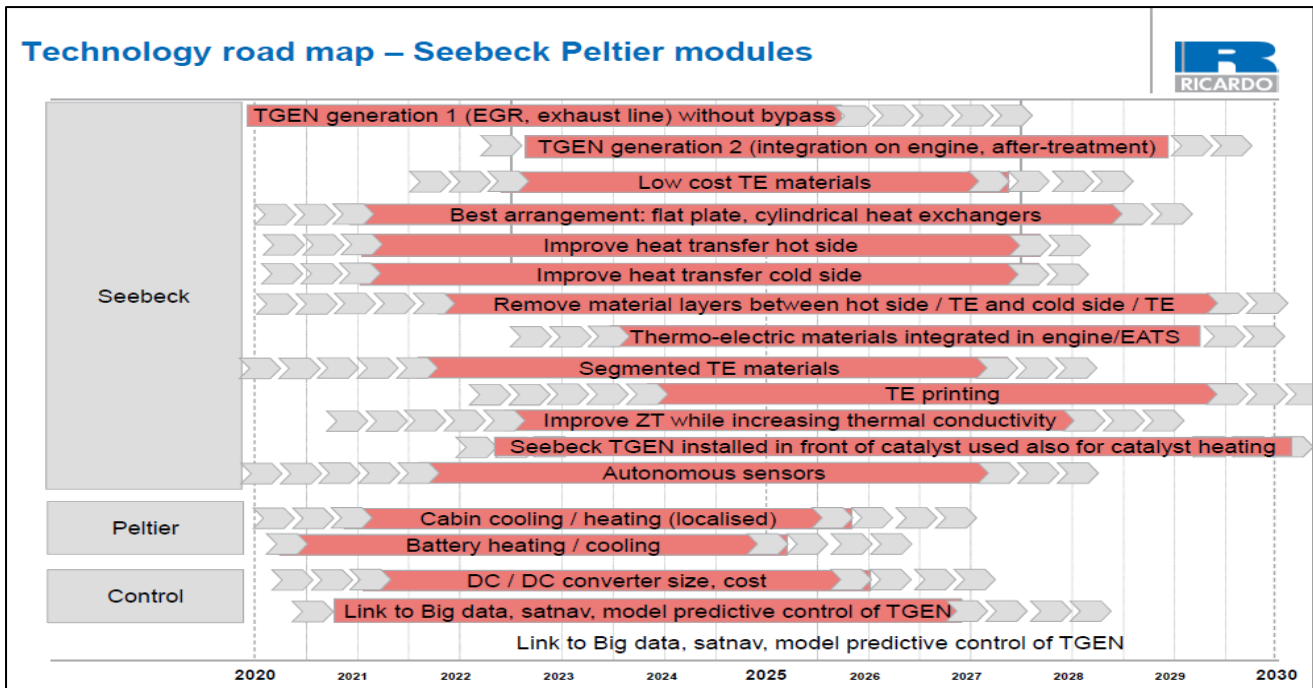
Figure 11: Roadmap for TEGs and Peltier Devices for Automotive sector (Courtesy of Ricardo 2017)

Power range opportunities: a few hundreds of kW or higher

The traditional high-heat producing industries such as cement, steel and glass offer clear opportunities for energy harvesting although the proportion of national energy consumption is now less than for domestic space-heating. The retail and service sectors offer interesting opportunities for heat management using TEGs where, for example, heat produced from refrigeration units is presently untapped for energy scavenging.

6.4.3 Consumer/IoT/Medical/Sensors

Power range opportunities: mW or less

For consumer-based electronics, IoT and sensor networks, energy scavenging options are of interest in prolonging battery life or even dispensing with batteries altogether. In applications where self-powering sensors are needed then the existence of a temperature gradient, large or small, can be sufficient to power

periodic or continuous data transmission for a wide range of uses including the fast growing home-care sector and could be exploited in the medical sector.

6.4.4 Multi-Sector

Power range opportunities: mW to MW

Table 4 Shows examples of opportunities for thermoelectric harvesting and the potential range of industry sectors which could benefit. The list is not exhaustive but demonstrates the wide variety of applications with power ranges from mW to MW.

Table 4: Examples of Opportunities for TE Harvesting & Cooling showing the potential range of industry sectors which could benefit [73]

Opportunity	Sector
Exhaust gas heat recovery for fuel efficiency	Automotive
Heat shielding & cooling	Automotive
Heat recovery for powering electrical systems	Aerospace
Airframes- thermal management	Aerospace
Heavy duty marine heat harvesting	Marine
Food distribution & in-store chillers	Retail/Food
Personal and space cooling	Consumer / Buildings
Recovery of heat in energy intensive process industries	Manufacturing
Cooling of electronics	Electronics
Powering of wearable electronics & sensors for health	Healthcare
Powering Wireless Sensor Networks	Internet of Things
Combined Heat & Power - Increase electrical efficiency	Energy
Solar heat harvesting	Energy
Geothermal heat harvesting	Energy

6.5   Thermoelectric Roadmaps to 2040

Figure 12 shows a long term thermoelectric Roadmap developed by Kajikawa in 2012 [74] focussing on applications sections with projected developments in efficiency. Figure 13 shows a long term thermoelectric Roadmap developed by the Thermoelectric Society of Japan [75]. Three phases are envisaged for the development of materials and systems over a period of 20 years.

Figure 12. Thermoelectric Roadmap – developed by T Kajikawa, Shonan Institute of Technology, Japan [74].

Figure 13. Thermoelectric Roadmap – adapted from work by Thermoelectric Society of Japan [74].

7.   RECOMMENDATIONS (for Policy Makers and Other Stakeholders)

To enable the UK to reap the benefits from initial developments and be able to exploit the growing market and opportunities for thermoelectrics it is recommended that there should be investment and support for a new generation of thermoelectric materials that exploits the synergies between experimental and computational expertise, novel device architectures, associated novel manufacturing and materials preparation techniques and system integration, namely:

(i) Theoretical, modelling and experimental investigations of materials at the nanoscale to develop strategies to design material nanostructures giving significantly improved ZT performance. This could for instance be encouraged through a specific funding call from RCUK or associated funding agencies aimed at fundamental studies such as those described in this document. Such a call would help maintain the tremendous momentum built through the Research Network initiative.

(ii) Development of next generation of thermoelectrics by incorporating advances in nanotechnology (including nano-structuring, 2-D layered materials, graphene and graphene-like) that promise performance improvements beyond bismuth telluride. This could be encouraged by fostering further collaborations with nano-technology focused groups, though, e.g. cross-departmental collaborations within higher education/research institutions.

(iii) Development of novel high performance TE materials composed of earth-abundant elements to meet current and developing needs (sectors will include automotive, heavy industry, aerospace, marine and nuclear), with an emphasis on maximising the average value of the figure of merit (ZT) rather than the maximum value.

(iv) Application of advanced manufacturing techniques to improve the production of thermoelectric generators through new materials processes including printing, additive layer manufacturing, and adaptation of semiconductor industry processing tools.

(v) A round robin sample exchange and calibration effort within the U.K. thermoelectric materials community to establish and validate the performance data and the reasons for differences in the data; this should include both bulk and thin film materials. The results of this community effort would be presented at international meetings on thermoelectrics and published as a 'consortium' scientific contribution

(vi) Focussed effort to understand and overcome packaging and interface issues, including thermally-induced mechanical stresses, limiting thermoelectric performance, long-term stability and durability.

(vii) Development of integrated manufacturing processes that facilitate the routine assembly of novel device architectures to match the shape of the heat source, and address heat transfer aspects including heat-exchangers.

(viii) Devices tailored for the very wide range of applications from body sensors, medical devices and IoT to industrial plant, trucks and jet engines.

(ix) An industrial network covering solid-state heating and cooling be set up to promote information exchange and collaboration, to identify opportunities for synergy across different end-use sectors, which links-in with the academic sector.

(xi) Support for demonstrator-projects that encompass materials scale-up through to prototype system testing, and exploitation of novel high-performance materials in a cost-effective manner

(x) Support for funding instruments to enable an integrated approach to thermoelectric activities thereby strengthening the UK R&D community.

8. THERMOELECTRIC ACTIVITIES – Profiles: UK Industry and Academe

8.1 UK Industry

8.1.1 BAE Systems Military Aircraft and Information (MAI), Warton

BAE Systems Military Aircraft and Information (MAI) at Warton are considering various potential applications for thermoelectrics on future combat aircraft projects. Example applications of interest include:

- Future aircrew clothing - multiple applications of integral novel materials / devices within fabric.
- Supplementary Electrical power generation from propulsion jet pipe.
- Incorporation of thermoelectrics within certain Heat Exchangers to enhance system performance

Investigations on the first two topics are at an early proposal stage whilst for the third, a number of practical demonstrations at initial proof-of-concept level have taken place. A research demonstration has also been done applying thermoelectrics to the installation of equipment requiring cooling in aircraft avionics bays

8.1.2 Cambridge Display Technology, Cambridge

CDTs research into thermoelectrics is focussed on the development of flexible, printable thermoelectric generators for the harvesting of low grade heat to power autonomous sensors, wearable electronics and other small electronic devices. CDT is engaged in the development of both n- and p-type novel printable materials for thermoelectrics as well as processes and devices which enable high performance whilst maintaining the durability and practicality that a flexible device offers.

Current limitations to the widespread adoption of printable and flexible thermoelectrics include:

- Lower electrical conductivity of materials relative to their bulk counterparts, especially of n-type materials. Seebeck and thermal conductivity are currently comparable or better than bulk materials, once electrical conductivity is increased material ZT approaching 1 should be possible.
- Increased module power towards 1 mW cm^{-2} (ΔT = 20K) over the next 5 years which can be enabled by better materials and improved flexible module design.
- Development of manufacturing capability for flexible and novel thermoelectrics especially within the UK.

8.1.3 European Thermodynamics, Kibworth

European Thermodynamics Ltd. was established in 2001. It specialises in thermal modelling and analysis and in the design, manufacture and supply of thermal management products for enclosure-based electronics and electrical equipment. Products range from Peltier and power generating thermoelectric modules to complete cooling assemblies and thermal controller units.

The company is currently involved in a number of InnovateUK and EU Horizon 2020 funded projects. Current research and development projects include: JOSPEL: A Novel Energy-efficient Electric Vehicle Climate

System; COACH: Advanced glasses, Composites and Ceramics for High growth Industries - European Training Network (ETN); VIPER2: Re-examining the Use of Thermal Energy in Engine Management; TRIUMPHANT: Improved Performance Phase Change Thermal Interface Material; and DUET: Heavy Duty, Dual Fuel, Demonstrator Engine Achieving Future EU Emissions Compliance with 23% Carbon Reduction

The company uses the latest mechanical modelling software as well as having in-house test and prototyping capabilities. Its latest investment is in state of the art pilot line production facilities for the development of custom and novel thermoelectric devices.

8.1.4 Linseis, Selb, Germany

Linseis manufactures and sells multiple devices in the field of thermal analysis and thermal physical property measurements. This includes the most complete instrument range for measurement of thermoelectrically relevant properties such as thermal conductivity, thermal diffusivity, specific heat, Hall effect, Seebeck effect and electric resistivity.

LSR-3 and 4 provide market leading Seebeck effect and electric resistivity determination of bulk and thin-film samples. Linseis also supplies a broad range of laser flash analyzers for determination of thermal diffusivity, thermal conductivity and specific heat (comparative method). Up to 18 samples can be measured at the same time, while samples as small as 3 x 3 mm can be characterised. The instrument portfolio also includes thin-film characterization systems capable of measuring films in the nm to μm range using a pre-structured chip onto which the film is deposited. Linseis has a significant presence in the UK market in collaboration with SemiMetrics Ltd, a research performing SME. The companies have joint collaborations with several UK Universities working in the field of thermoelectric materials research.

8.1.5 Johnson Matthey PLC

Johnson Matthey (JM) is an advanced materials and catalysis company manufacturing a wide range of products for industry from pharmaceuticals to battery components. We are a leading supplier of emission control catalysts and many end-user applications, for example in the automotive sector, have scope for recovery of energy from waste heat. Thermoelectrics technology is an opportunity for us to provide both existing and new customers with a materials-based solution for energy recovery or harvesting. Accordingly, we have recently invested in a measurement and processing lab to carry out R&D into advanced thermoelectric materials for module components and thermal interface brazes. JM has both the manufacturing capability and intent to be part of any appropriate supply chain in the global thermoelectrics market.

8.1.6 Netzsch, Selb, Germany

NETZSCH Analyzing and Testing is a division of the NETZSCH group, specializing in thermal analysis, adiabatic reaction calorimetry and the determination of thermophysical and thermoelectrical properties.

The Seebeck analyzer SBA 458 Nemesis allows for more sample geometries than usual for this technique and measurements can be carried out between room temperature and 1100 °C. Thermal analysis instrumentation can be used to determine likely maximum service temperatures of TE devices and the analysis of phase transitions or the specific heat capacity (C_p). Instrumentation can be supplied to characterize the thermal and volumetric expansion of materials and their density change, allowing for the analysis and prediction of thermal stresses in a real device.

The laser flash (LFA) technique is a fast, non-contact, absolute method for determining a complete set of thermophysical properties, including thermal diffusivity, specific heat capacity and thermal conductivity. For thin layers on non-transparent substrates, thermoreflectance methods are preferred through the pulsed light NanoTR/PicoTR instruments. In addition to instrumentation, Netzsch provides complementary software modules (thermokinetics, thermal simulations, component kinetics, peak separation and purity), Netszch has a significant presence in the UK market

8.1.7 Ricardo, Shoreham by Sea

Efficient and cost-effective energy recovery from the exhaust gases of internal combustion engines is a high priority for automotive manufacturers. In order to meet future CO_2 and pollutant emissions legislation significant research effort is needed to increase fuel efficiency and improve exhaust after treatment thermal management. No single advance will yield the performance gains sought: a range of measures will be needed, optimised for engine applications and fuel types.

Ricardo are a world leader in automotive technology development and recognise that thermoelectrics provide significant commercial opportunities for automotive vehicles and powertrains both in regards of waste heat recovery and for the integration of heating and cooling systems for vehicle thermal comfort and electric components thermal management.

As a leading global automotive consulting group, we are continually striving to develop and apply advanced technologies. We see the application of low cost, high temperature thermoelectric systems as being of very high importance in future vehicle platforms. Longer term, to support the commercial impacts, we have identified a clear requirement for significant device capacity with mid to high temperature capability.

Ricardo are involved in long term developments relating to the development of thermoelectric generators for automotive waste heat recovery systems and have already undertaken a number of internally and externally funded projects to accelerate the implementation of thermoelectric generators for automotive application.

To successfully commercialise thermoelectric systems the major challenge is reducing the materials cost whereby currently this cost frequently dominates the total system cost. This cost must be addressed before a viable system can be produced. If a low cost, high performance, high reliability material and device can be produced in a scalable manner, this will be a major step for UK universities and companies involved in such Research and Advanced Engineering activities.

Ricardo have identified if this is achieved then uptake for thermoelectric systems could viably begin during 2020/2022 time frame, but this is reliant on this important material and device step being addressed.

8.1.8 Rolls Royce, Derby

Rolls-Royce visualise three potential application areas for thermoelectric (TE) materials: (1) as a power supply for distributed wireless sensor networks; (2) in the dual role of power supply and thermal management for embedded instrumentation and monitoring devices; and (3) the thermal management of engine components under operational conditions. Themes (1) and (2) are of immediate interest; (3) was

mooted some time ago and widely discussed in the aerospace sector but so far there is no significant research and development impetus.

Wireless sensor networks offer the manufacturing and cost advantage of reductions to parts count and mass and the flexibility to allow upgrade or modification with a minimum of disruption. During maintenance work the installed network can be augmented with a special purpose additional network able to supplement and refine engine data.

Specific TE materials are of interest to Rolls-Royce only insofar as new materials with improved ZT give better performance in the engine thermal environment. However concern continues over the difficulty of generating the required device temperature difference to give a practical power output appropriate to the requirements of sensors. Start-up in cold environments raises the issue of supplementary power supplies or the need for "hybrid" vibration/TE devices that scavenge both mechanical and thermal sources depending on their working environment.

In the marine business of Rolls-Royce, there is interest in energy recovery which is focussed primarily on supplementary thermodynamic cycles. Health monitoring as an aspect of "ship intelligence" offers another potential application area for TE devices that provide a power supply for sensors networks. Marine engines and shipboard conditions offer better potential for creating the needed temperature gradients.

8.1.9 SemiMetrics Ltd, Kings Langley

SemiMetrics Ltd is an SME with a long track record of involvement in semiconductor material characterisation and metrology. We are a "research performing" SME working on joint developments with several UK Universities and are a commercial partner in several EPSRC funded research consortia. SemiMetrics Ltd is currently developing thermoelectric characterisation techniques providing consultation services to larger manufacturing companies to deliver commercial products world-wide. In the field of thermal analysis and thermoelectrics our partner is Linseis Messgeräte GmbH, based in Selb, Germany. Our companies offer a range of bulk and think film thermoelectric characterisation products. In the UK, we are the market leading supplier of thermoelectric measurement instruments

8.1.10 Thermoelectric Conversion Systems Ltd, Glasgow

Thermoelectric Conversion Systems Ltd is a Scottish technology SME who specialise in the electronic and thermal design of thermoelectric systems for power generation and cooling. The business comprises four main areas: (i) *Electrical power conditioning*; Electronic systems incorporating software algorithms to enable the operation at the Maximum Power Point (MPP) or Maximum Coefficient of Performance (MCoP) to condition the electrical output power from thermoelectric generators and the input power to thermoelectric coolers. (ii) *Device characterisation*; Using in-house test equipment and expertise we undertake the design and measurement of a wide range of thermoelectric systems and components. (iii) *Thermoelectric Module Supply*; TCS Ltd has developed high temperature modules optimised for power generation from combustion engine exhaust gas systems. The 40 mm x 40 mm device can generate over 20 W of electrical power at 16V. (iv) *Educational products*: A suite of laboratory products that includes equipment to demonstrate both heat pumping and power generation from thermoelectric materials and devices.

8.2 Academe

TE research activities of the UK community are summarised below, with in each case three key references to recent work

8.2.1 University of Bath – Prof. Stephen C. Parker

We are exploiting computational approaches to evaluate the relationship of structure, lattice dynamics and defect properties with a material's usefulness for thermoelectric applications. Hence we aim to elucidate ways for their improvement and provide predictions for complementary experiments. Amongst the promising n- and p-type thermoelectric oxide materials that we have investigated are misfit layered cobalt oxides $(M_2CoO_3)_{0.6}CoO_2$ (M = Mg, Ca, Sr, Ba) and $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$ (BSCO), perovskite $CaMnO_3$, tungsten bronze $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ceramics, where we investigated the role of stoichiometry. One important way of improving the thermoelectric efficiency is by reducing the thermal conductivity, and hence we have explored the effect of nanostructuring of the prototypical n-type material, $SrTiO_3$, as well as the potential of application of displacive instabilities in chalcogenides. Most recently, we have been investigating hybrid materials in the search for better ways of decoupling and controlling electronic and thermal properties in thermoelectric materials.

- SR Yeandel, M Molinari, SC Parker, Nanostructuring perovskite oxides: the impact of $SrTiO_3$ nanocube 3D self assembly on thermal conductivity, RSC Advances, 6, 114069-114077, (2016)
- JD Baran, D Kepaptsoglou, M Molinari, N Kulwongwit, F Azough, R Freer, QM Ramasse, SC Parker, Role of Structure and Defect Chemistry in High-Performance Thermoelectric Bismuth Strontium Cobalt Oxides, Chemistry of Materials, 28, 7470-7478, (2016)
- M Molinari, DA Tompsett, SC Parker, F Azough, R Freer, Structural, electronic and thermoelectric behaviour of $CaMnO_3$ and $CaMnO_{(3-\delta)}$, Journal of Materials Chemistry A, 2, 14109-14117, (2014)

8.2.2 Cardiff University – Prof. Gao Min

The Cardiff Thermoelectric Laboratory, established by Prof D M Rowe in 1967, is one of 3 groups in the world that have continuous thermoelectric research since the 1960s (the other 2 are JPL and Ioffe Institute). Fine-grain SiGe developed at Cardiff (1981) pioneered nano-engineering of phonons. The waste heat recovery programme funded by Japanese NEDO (1994) was the first large-scale project in thermoelectric waste heat recovery that signposted the recent resurgence of interest in thermoelectrics. The Cardiff group is also credited for setting new directions in thermoelectric research including electron energy filtering (1994) and integrated micro TE converters (1998). Current research activities at Cardiff focus on developing high temperature TE modules, novel dual I-V curve technique for module performance evaluation, thermoelectric impedance spectroscopy, a high-throughput thermoelectric property testing facility, and hybrid PV/TE systems.

- J Garcia-Canadas, AV Powell, A Kaltzoglou, P Vaqueiro, G Min, Fabrication and evaluation of a skutterudite-based thermoelectric module for high temperature applications, Journal of Electronic Materials, 42, 1369-1374, (2013)
- G Min, "Principle of Determining Thermoelectric Properties Based on I-V Curves" Measurement Science & Technology, 25, 1-6, (2014)
- J Garcia-Canadas, G Min, Multifunctional probes for high-throughput measurement of Seebeck coefficient and electrical conductivity at room temperature, Review of Scientific Instruments., 85, 043906, (2014)

8.2.3 University of East Anglia - Dr Yimin Chao

Dr Yimin Chao has an established track record in investigating nanostructured systems from the basic physical and chemical mechanisms of synthesis, through their optical and electronic properties to scientific

and industrial applications. His work has attracted funding from the EPSRC, Royal Society, Leverhulme Trust, EU framework 7, and Industry in the past five years. His recent research interests are focused on synthesis of magnetic nanocomposite thermoelectric materials with magnetic nanoparticles to investigate the magnetoelectric effect, engineering band structure of thermoelectric materials to enhance the thermoelectric performance, and hybrid nanoparticles for flexible thermoelectric applications.

- W Zhao, Z Liu, P Wei, Q Zhang, W Zhu, X Su, X Tang, J Yang, Y Liu, J Shi, Y Chao, S Lin, Y Pei, Magnetoelectric interaction and transport behaviours in magnetic nanocomposite thermoelectric materials, Nature Nanotechnology, 12, 55–60 (2017)
- J Cui, M Cheng, W Wu, Z Du, Y Chao, Engineering band structure via the site preference of Pb^{2+} in the In^{+} site for enhanced thermoelectric performance of In_6Se_7, ACS Applied Materials and Interfaces, 8, 23175–23180, (2016)
- SP Ashby, JA Thomas, J Garcia-Canadas, G Min, J Corps, AV Powell, H Xu, W Shen, Y Chao, Bridging silicon nanoparticles and thermoelectrics: phenylacetylene functionalization, Faraday Discussions, 176,349–361, (2014)

8.2.4 University of Exeter – Prof. GP Srivastava

The modelling work at University of Exeter seeks to identify the key parameters for developing the phonon engineering of Si-based nanocomposite thermoelectric materials by undertaking a systematic state-of-the-art theoretical study of their enhanced ZT over a wide temperature range. The investigations have shown, in agreement with previous studies, that the thermoelectric figure of merit (ZT) of a heavily doped Si-Ge alloy takes a maximum value of less than 1 at around 1000 K. Interestingly, it was predicted that for a heavily doped ultra-thin Si/Ge superlattice, an enhancement in ZT to a value between 3 and 6 can be achieved over the broad temperature range 400-1200 K. The theoretical investigation highlighted the important role of increased phonon interface scatterings in ultrathin superlattices in achieving a significant reduction in the phonon conductivity.

- IO Thomas, GP Srivastava, Lattice thermal conduction in ultra-thin nanocomposites, Journal of Applied Physics, 119, 244309, (2016)
- GP Srivastava, Tuning phonon properties in thermoelectric materials, Reports on Progress in Physics, 78, 026501, (2015)
- IO Thomas, GP Srivastava, Tuning phonon properties to enhance the thermoelectric figure of merit, AIP Conference Proceedings, 1590, 95-104, (2014)

8.2.5 University of Glasgow – Prof. Duncan Gregory

A key component of the research portrfolio of The Inorganic Solid State Materials Group at the School of Chemistry, University of Glasgow is the study of *new thermoelectric materials*. This research concerns the design and discovery of bulk and nanoscale materials and notably the chemistry and physics of metal chalcogenides. Gas-solid approaches (e.g. CVT, CVD) and solution processes have been exploited to produce 1D nanowires and 2D nanosheets with improved electronic transport properties and reduced thermal conductivity. An understanding of the growth and functionality of these solids has been gleaned using diffraction, electron microscopy, spectroscopy and a suite of property measurement techniques.

- Y Zhao, RW Hughes, Z Su, W Zhou, DH Gregory, One-step synthesis to 2D structures of bismuth telluride, Nanosheets of a Few Quintuple Layers in Thickness. Angewandte Chemie International Edition, 50, 10397-10401, (2011)
- G Han, SR Popuri, HF Greer, JW-G Bos, W Zhou, AR Knox, A Montecucco, J Siviter, EA Man, M Macauley, DJ Paul, W Li, MC Paul, G Min, T Sweet, R Freer, F Azough, H Baig, N Sellami, TK Mallick, DH Gregory, Facile

Surfactant-Free Synthesis of p-type SnSe Nanoplates with Exceptional Thermoelectric Power Factors., Angewandte Chemie International Edition, 55, 6433 – 6437 (2016)

- G Han, SR Popuri, HF Greer, LF Llin, JWG Bos, DJ Paul, W Zhou, H Ménard, AR Knox, A Montecucco, J Siviter, EA Man, W Li, MC PC Manosh, G Min, T Sweet, R Freer, F Azough, H Baig, TK Mallick, DH Gregory, Chlorine-Enabled Electron Doping in Solution-Synthesised SnSe Thermoelectric Nanomaterials., Advanced Energy Materials, 7, 1602328, (2017)

8.2.6 University of Glasgow – Prof. Doug Paul

The research interests of the group in the School of Engineering include nanofabrication, quantum technologies, Si/SiGe heterostructures, nanoelectronic silicon devices, quantum cascade lasers, quantum devices, silicon photonics, plasmonics for mid-infrared applications, terahertz systems, sensors and elemental thermoelectrics, particularly nanoscale devices.

- D Alonso-Alvarez, L Ferre Llin, A Mellor, DJ Paul, NJ Ekins-Daukes, ITO and AZO films for low emissivity coatings in hybrid photovoltaic-thermal applications, Solar Energy, 155, 82-92 (2017)
- VP Georgiev, MM Mirza, AI Dochioiu, FA Lema, SM Amoroso, E Towie, C Riddet, DA MacLaren, A Asenov, DJ Paul, Experimental and simulation study of 1D silicon nanowire transistors using heavily doped channels, IEEE Transactions on Nanotechnology, 16, 717-735, (2017)
- L.F. Llin, DJ Paul, Thermoelectrics, Photovoltaics and Thermal Photovoltaics for Powering ICT Devices and Systems, ICT-Energy Concepts for Energy Efficiency and Sustainability, INTECH, 215-237, (2017)

8.2.7 University of Glasgow – Prof. Andrew Knox

The Thermoelectric Systems Group in the School of Engineering specialises in the design of power converters, MPPT algorithms for TEGs and the electrical and thermal characterisation of modules under constant temperature and constant heat conditions. This knowledge is applied to a range of thermoelectric systems from the mW level for environmental energy harvesting to multi-kW output from exhaust gas waste heat systems. The group has developed a wide range of automated test and measurement equipment able to replicate real-world system operating conditions for single devices and multi-TEG arrays in a hot gas flow.

- A Montecucco, J Siviter, AR Knox, Constant Heat Characterisation of Thermoelectric Generators and Optimisation of Pellets Packing Factor, Applied Energy, 149, 248–258, (2015)
- A Montecucco, J Siviter, AR Knox, The Effect of Temperature Mismatch on Thermoelectric Generators Electrically Connected in Series and Parallel, Applied Energy, 123, 47-54, (2014)
- A Montecucco, AR Knox, Accurate simulation of thermoelectric power generating systems, Applied Energy, 118, 166–172, (2014)

8.2.8 Heriot-Watt University - Dr Jan-Willem Bos

The Energy Materials Group at Heriot-Watt University is focused on the synthesis and characterisation of inorganic thermoelectric materials. Our main interest is in intermetallic Zintl-type materials with the half-Heusler structure with some work on other materials classes, including transition metal oxides and chalcogenides. Our work combines solid-state synthesis, detailed structural investigations, including a large amount of work at the UK and EU synchrotron and neutron sources, and careful property measurements. In terms of our laboratory infrastructure, we have a wide range of synthetic equipment, including an arc-melting furnace, and have equipment to measure the thermoelectric parameters between room-temperature and 800 °C for resistivity and Seebeck coefficient and up to 1500 °C for thermal conductivity.

- SR Popuri, M Pollet, R Decourt, FD Morrison, NS Bennett, JWG Bos, Large thermoelectric power factors and impact of texturing on the thermal conductivity in polycrystalline SnSe, Journal of Materials Chemistry C, 4, 1685-1691 (2016).

- RA Downie, RI Smith, DA MacLaren, JWG Bos, Metal Distributions, Efficient n-Type Doping, and Evidence for in-Gap States in TiNiM$_y$Sn (M = Co, Ni, Cu) half-Heusler Nanocomposites, Chemistry of Materials, 27, 2449-2459 (2015)
- RA Downie, DA MacLaren, JWG Bos, Thermoelectric performance of multiphase XNiSn (X = Ti, Zr, Hf) half-Heusler alloys, Journal of Materials Chemistry A, 2, 6107-6114 (2014)

8.2.9 Heriot-Watt University – Dr Nick Bennett

The Nanomaterials Lab at Heriot-Watt University has active thermoelectric research in the area of silicon-based bulk- and nano-materials, such as nano-films, nano-wires and nano-crystalline thin-films. Our principal interest is in silicon defect-engineering – such as so-called "vacancy-engineering" – as a novel approach to silicon-based thermoelectrics. Other defect-engineering strategies for silicon thermoelectrics being explored by the group includes the creation of nano-scale dislocation loops, which we have shown can greatly enhance the thermoelectric power factor in Si nanowires and Si nano-films. Our work includes attempts to up-scale these methods beyond the nano-scale, to firstly, thin-films, and ultimately to bulk materials.

- NS Bennett, NM Wight, SR Popuri, JWG Bos, Efficient thermoelectric performance in silicon nano-films by vacancy-engineering, Nano Energy, 16, 350-356 (2015)
- NS Bennett , D Byrne, A Cowley, Enhanced Seebeck coefficient in silicon nanowires containing dislocations, Applied Physics Letters, 107, 013903 (2015)
- NM Wight, NS Bennett, Reduced Thermal Conductivity in Silicon Thin-Films via Vacancies, Solid State Phenomena, 242, 344-349 (2016)

8.2.10 Imperial College London – Prof. Aaron Walsh

The group of Aron Walsh at Imperial College London has been developing computational methods to understand and control phonon-phonon interactions in solids. They identified a structural instability at the heart of the high performance of SnSe thermoelectrics, have shown how phonon lifetime can be modified from binary to quaternary semiconductors, and have predicted ultra-low thermal conductivity in hybrid halide perovskites, which act as phonon-glass electron crystals.

- JM Skelton, LA Burton, SC Parker, A Walsh, C Kim, A Soon, J Buckeridge, A Sokol, CRA Catlow, A Togo, I Tanaka, Anharmonicity in the high-temperature Cmcm phase of SnSe: soft modes and three phonon interactions. Physical Review Letters, 117, 75502 (2016)
- T Shibuya, J Skelton, A Jackson, K Yasuoka, A Togo, I Tanaka, A Walsh. Suppression of lattice thermal conductivity by mass-conserving cation mutation in multi-component semiconductors, APL Materials, 4, 104809, (2016)
- LD Whalley, JM Skelton, JM Frost, A Walsh, Phonon anharmonicity, lifetimes, and thermal transport in $CH_3NH_3PbI_3$ from many-body perturbation theory, Physical Review B, 94, 220301, (2016)

8.2.11 King's College London - Dr Nicola Bonini

His interests concentrate on understanding and engineering the electrical and thermal transport properties of complex materials for thermoelectric applications. For this he has developed techniques to solve the Boltzmann transport equation (for electrons and phonons) where the carriers' scattering rates (electron-phonon and phonon-phonon interactions) are computed fully from first-principles. This approach is free of adjustable parameters and provides direct access to all the thermoelectric coefficients, also including the effect of nonequilibrium phonon populations induced by temperature gradients (phonon drag effect). He is currently working on the transport properties of silicon-based materials as well as of copper-based sulphide thermoelectric compounds, also focussing on defect properties and structural stability.

- K Chen, B Du, N Bonini, CWeber, HYan, MJ Reece, Theory-guided synthesis of an eco- friendly and low-cost copper-based sulfide thermoelectric material, The Journal of Physical Chemistry C, 120, 27135-27140, (2016)
- M Fiorentini, N Bonini, Thermoelectric coefficients of n-doped silicon from first-principles via the solution of the Boltzmann transport equation, Physical Review B, 94, 085204, (2016)
- J Garg, N Bonini, B Kozinsky, N Marzari, The role of disorder and anharmonicity in the thermal conductivity of silicon-germanium alloys: a first-principles study, Physical Review Letters, 106, 045901, (2011)

8.2.12 King's College London – Dr Cedric Weber

His interests concentrate on understanding the electronic properties of correlated materials. He has developed techniques to overcome the limitations of density functional theory in the class of strongly correlated materials (transition metal oxides and sulphides, chalcogenides), in particular via the DMFT and GW approaches. The DMFT approach allows describing the underlying electronic structures of correlated oxides, both for the ground state and excited states. He has derived within this formalism a new theory to compute the Seebeck coefficients. He is one of the developers of the CASTEP and ONETEP DFT codes, the two leading codes in the UK. He is currently working on implementing DMFT within the CASTEP code.

- W Xu, C Weber, G Kotliar, High-frequency thermoelectric response in correlated electronic systems, Physical Review B, 84 , 035114, (2011)
- L Sponza, P Pisanti, A Vishina, D Pashov, C Weber, M van Schilfgaarde, Self-energies in itinerant magnets: A focus on Fe and Ni, Physical Review B, 95, 041112, (2017)
- C Weber, DD O'Regan, NDM Hine, MC Payne, G Kotliar, PB Littlewood , Vanadium dioxide: A Peierls-Mott insulator stable against disorder, Physical Review Letters 108, 256402, (2012)

8.2.13 University of Lancaster – Prof. Colin Lambert

Research interests include nanoelectronics, single-molecule electronics and thermoelectric processes, quantum transport, quantum sensors, low-dimensional systems, graphene, silicene, carbon nanotubes, surface science, materials, magnetism, spintronics, superconductivity, density functional theory, non-equilibrium Greens functions, molecular dynamics, enhanced oil recovery, chemical sensing, nanomotors, DNA sequencing, surfactant design, micelle formation, surface coatings, transition-edge sensors,

- M Famili, I Grace, H Sadeghi, CJ Lambert, Suppression of Phonon Transport in Molecular Christmas Trees Chemical Physics and Physical Chemistry, 18, 1234-1241, (2017)
- M Noori, H Sadeghi, CJ Lambert, High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires, Nanoscale, 9, 5299-5304, (2017)
- QH Al-Galiby, H Sadeghi, DZ Manrique, CJ Lambert, Tuning the Seebeck coefficient of naphthalenediimide by electrochemical gating and doping, Nanoscale, 9, 4819-4825, (2017)

8.2.14 University of Leicester – Dr Hugo Williams and Prof. Richard Ambrosi

The University of Leicester is leading the development of radioisotope power systems for potential future European space missions. The Leicester team have achieved the first demonstration of a representative laboratory prototype for a Radioisotope Thermoelectric Generator (RTG) designed for Am-241 fuel. Leicester's thermoelectric expertise is in characterising the mechanical performance of thermoelectric materials (e.g. micro & nano-hardness, flexural strength and fracture toughness), using impedance spectroscopy to characterise the thermoelectric performance of modules and measuring the emergent performance of thermoelectrics when integrated into practical aerospace and high-performance systems. These developments have been driven by the development of RTG prototypes but will be equally applicable to terrestrial application of thermoelectric conversion. Leicester's thermoelectrics activities are interdisciplinary, involving staff based in both the Departments of Physics & Astronomy and in Engineering, and involve collaboration with companies and universities in Europe and the USA.

- HR Williams, RM Ambrosi, K Chen, U Friedman, H Ning, MJ Reece, MC Robbins, K Simpson, K Stephenson, Spark plasma sintered bismuth telluride-based thermoelectric materials incorporating dispersed boron carbide, Journal of Alloys and Compounds, 626, 368-374 (2015)
- R Mesalam, HR Williams, RM Ambrosi, K Chen, MJ Reece, Enhanced Mechanical Properties in n-type Bi2Te3 Prepared by FAST-Deformation Processing. Proceedings of Nuclear and Emerging Technologies for Space, Orlando, USA, 2017
- R Mesalam, HR Williams, RM Ambrosi, DP Kramer, CD Barlay, J García-Cañadas, K Stephenson, Impedance Spectroscopy of Neutron Irradiated Bi2Te3 Based Thermoelectric Modules for RTG Environments, Proceedings of Nuclear and Emerging Technologies for Space, Orlando, USA, 2017

8.2.15 University of Liverpool - Dr Jonathan Alaria

Group activity related to thermoelectricity focuses on the preparation and characterisation of materials for thermoelectric applications. This activity can be classified in three different areas: (i) *New oxide thermoelectric for high temperature applications*: we have recently started to investigate the thermal and electrical properties of compounds based on the trirutile family. This project focuses on the preparation of polycrystalline materials and their physical characterisation (electrical conductivity, thermal conductivity and thermopower) from 2K to 1000 K. (ii) *Spincaloritronics:* we are developing methods to measure the magneto-thermal effect (Nernst-Etthinghausen), in particular exploring the origin of the spin-Seebeck effect in low dimensional magnets. The materials produced in this project are large single crystals. (iii) *Sulfides and Selenides for Te replacement:* we are synthesising and characterising complex inorganic sulphides and selenides which should operate in the ambient temperature region.

- WM Linhart, MK Rajpalke, J Buckeridge, PAE Murgatroyd, JJ Bomphrey, J Alaria, TD Veal, Band gap reduction in InN_xSb_{1-x} alloys: Optical absorption, k·P modeling, and density functional theory, Applied Physics Letters, 109, 132104, (2016)
- P Mandal, MJ Pitcher, J Alaria, H Niu, M Zanella, JB Claridge, MJ Rosseinsky, Controlling Phase Assemblage in a Complex Multi-Cation System: Phase-Pure Room Temperature Multiferroic $(1-x)BiTi_{(1-y)/2}Fe_yMg_{(1-y)/2}O_{3-x}CaTiO_3$, Advanced Functional Materials, 26, 2523-2531, (2016)
- M O'Sullivan, J Hadermann, MS Dyer, S Turner, J Alaria, TD Manning, MJ Rosseinsky, Interface control by chemical and dimensional matching in an oxide heterostructure, Nature Chemistry, 8, 347-353, (2016)

8.2.16 University of Liverpool – Prof. Matthew Rosseinsky

We work on the synthesis of new thermoelectric materials, in close collaboration with Jon Alaria (Liverpool Physics), and the computational groups of Matthew Dyer and George Darling (Liverpool) and Furio Cora and Ben Slater (UCL). The activity focusses on (i) New oxide thermoelectrics where we are studying the phonon glass-electron crystal materials produced by extensive disorder on the A site of the perovskite structure and (ii) New multiple anion materials with low thermal conductivities where new families of materials containing oxide, halide and chalcogenide materials have been identified that combine structural units characteristic of well-known thermoelectric families and have some of the lowest thermal conductivities reported. The approach is characterised by an integration of materials discovery, structural and property characterisation and computational prediction of structure and properties.

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- C Collins, M Dyer, M Pitcher, G Whitehead, M Zanella, P Mandal, J Claridge, G Darling, M Rosseinsky, Accelerated discovery of two crystal structure types in a complex inorganic phase field. Nature, 546, 280-284. (2017)

- Q Gibson, M Dyer, G Whitehead, J Alaria, M Pitcher, H Edwards, J Claridge et al. $Bi_4O_4Cu_{1..7}Se_{2..7}Cl_{0..3}$: Intergrowth of BiOCuSe and Bi_2O_2Se Stabilized by the Addition of a Third Anion, Journal of the American Chemical Society, 139, 15568-15571. (2017)

8.2.17 Loughborough University – Prof. Richard Stobart

The research group's interest in thermoelectrics developed from investigations into energy recovery from internal combustion engines with the objective of improving vehicle fuel economy. With thermoelectrics the group is investigating heat exchange methods, thermal and electric architectures, and the validation and evaluation of TEG performance in application environments. Working in co-operation with the Solid State Materials Group at Reading and the Thermoelectric Group at Cardiff, the Loughborough group has worked on heat exchange, modelling and engine applications for novel thermoelectric materials.

Initial experimental work was conducted using a passenger car engine for which a detailed model was validated and then used to project the performance of a skutterudite based TEG. The modelling work has been extended to include dynamic effects which are of particular importance in the accurate prediction of power generated in passenger car applications. Investigation of heat exchange design and the configuration of modules has led to results on the effectiveness of module deployment and the proposal for design guidelines for thermoelectric generators. The modelling work has also been applied to the understanding of how electrical power will be deployed in the passenger car, and to the development of a business model of the application of TEGs across the automotive sector to help meet carbon dioxide emissions legislation.

In the most recent work conducted by the Group, models have been used in real-time during experimental work on practical engines to predict the output of a TEG fully populated with skutterudite modules. Work continues to refine heat exchange design and modelling methods and the ability to predict real world behaviour of TEG systems.

- R Stobart, M Wijewardane, Z Yang, Comprehensive analysis of thermoelectric generation systems for automotive applications, Applied Thermal Engineering, 112, 1433–1444, (2017)
- L Song, Z Yang, R Stobart, The Potential of Thermoelectric Generator in Parallel Hybrid Vehicle Applications, SAE Technical Paper, 2017-01-0189, (2017)
- Z Yang, E Winward, S Lan, R Stobart, Optimization of the Number of Thermoelectric Modules in a Thermoelectric Generator for a Specific Engine Drive Cycle, SAE Technical Paper, 2016-01-0232 (2016)

8.2.18 University of Manchester – Prof. Robert Freer

Thermoelectric work at Manchester focuses on earth abundant materials, particularly oxides and silicides. The group exploits a variety of traditional and novel processing routes to control powder properties and final microstructures as a means to develop materials with enhanced thermoelectric properties. We work closely with the modelling group at Bath and the SuperSTEM laboratory to define and understand the effects of atom level features and structures on thermoelectric performance.

Recent work has concentrated on n-type materials including $SrTiO_3$, $CaMnO_3$, $Nd_{2/3}TiO_3$, tungsten bronze structured niobates, and p-type materials involving misfit layered cobaltites including $Bi_2Sr_2Co_2O_x$. Recognising that many thermoelectrics exhibit a relatively narrow thermal operating range at peak performance, we have sought ways to significantly widen the effective thermal widow. Composites based on $SrTiO_3$ and graphene have been developed with peak ZT up to 0.42, with significantly increased electrical conductivity and thermoelectric performance from room temperature to 650 °C.

- Y Lin, C Norman, D Srivastava, F Azough, L Wang, M Robbins, K Simpson, R Freer, IA Kinloch, Thermoelectric Power Generation from Lanthanum Strontium Titanium Oxide at Room Temperature through the Addition of Graphene, ACS Applied Materials and Interfaces, 29, 15898-15908, (2015)
- JD Baran, M Molinari, N Kulwongwit, F Azough, R Freer, DM Kepaptsoglou, QM Ramasse, SC Parker, Role of Structure- and Defect Chemistry in High-Performance Thermoelectric Bismuth Strontium Cobalt Oxides, Chemistry of Materials, 28, 7470-7478, (2016)
- D Srivastava, C Norman, F Azough, MC Schafer, E Guilmeau, D Kepaptsoglou, QM Ramasse, G Nicotra, R Freer, Tuning the thermoelectric properties of A-site deficient $SrTiO_3$ ceramics by vacancies and carrier concentration, Physical Chemistry Chemical Physics, 18, 26475-26486, (2016)

8.2.19 University of Nottingham – Prof. Simon Woodward

Simon Woodward has contributed to organic (acene-based) thermoelectrics since 2010. Together with our industrial and European collaborators we have successfully demonstrated radical ion organic TE materials and devices. Our programme in organic thermoelectrics has been supported by UK industry and an EU award which has led to collaborations with the Institute of Solid State Physics (University of Latvia) producing the first tetrathiotetracene (TTT) thin film TE device. With the University of Würzburg we have helped demonstrate the first single crystal TTT thermoelectric device. The potential cross-sectional power output of the latter is >10^3 times greater than the best polymer TE materials.

- S Woodward, M Ackermann, S Ahirwar, L Burroughs, MR Garrett, J Ritchie, J Shine, B Tyril, K Simpson, P Woodward, Straightforward Synthesis of 2- and 2,8-Substituted Tetracenes, Chemistry: A European Journal, 23, 7819-7824, (2017)
- F Huewe, A Steeger, K Kostova, L Burroughs, I Bauer, P Strohriegl, V Dimitrov, S Woodward, J Pflaum, Low-Cost and Sustainable Organic Thermoelectrics Based on Low-Dimensional Molecular Metals, Advanced Materials, 29, 1605682, (2017)
- K Pudzs, A Vembris, M Rutkis, S Woodward, Thin film organic thermoelectric generator based on tetrathiotetracene, Advanced Electronic Materials, 3, 1600429, (2017)

8.2.20 Queen Mary University of London – Prof. Mike Reece

Research at QMUL on inorganic thermoelectrics is focused on environmentally friendly materials based on earth abundant elements, which includes silicides and sulphides. The objectives are the discovery and understanding of new materials and developing new and scaleable processing routes to produce nanostructured and textured materials. This includes electric current and magnetic field assisted processing. We are pioneering the flash sintering (>5,000 C) of materials using Spark Plasma Sintering, known as Flash-SPS (FSPS). We are also working with collaborators to develop protective coatings to enable thermoelectric materials to be used at high temperatures in air.

- B Du, F Gucci, H Porwal, S Grasso, A Mahajan, MJ Reece, Flash spark plasma sintering of magnesium silicide stannide with improved thermoelectric properties, Journal of Materials Chemistry C, 5, 1514-1521, (2017)
- H Ning, GD Mastrorillo, S Grasso, B Du, T Mori, C Hu, Y Xu, K Simpson, G Maizza, MJ Reece, Enhanced thermoelectric performance of porous magnesium tin silicide prepared by pressureless spark plasma sintering, Journal of Materials Chemistry A, 3, 17426-174232, (2015)
- RZ Zhang, K Chen, B Dua, MJ Reece, Screening of Cu-S based thermoelectric materials using crystal structure features, Journal of Materials Chemistry A, 5, 5013-2019, (2017)

8.2.21 Queen Mary University of London - Dr Bob Schroeder, Dr Emiliano Bilotti, Dr Mark Baxendale and Dr Oliver Fenwick

The Organic Thermoelectric Laboratory at QMUL unites the synthesis, characterisation, processing and device activities of four research groups. Synthetic activities of this group focus on new n-type thermoelectric materials and self-doped materials. Characterisation covers bulk and thin film ZT

measurement and has been used to develop new models of thermoelectricity in established PEDOT materials. The group also seeks to understand the role of morphology, structure and self-assembly under doping conditions. Materials processing is key with activities on scalable processing through using polymer composite materials and by synthesis of new materials with enhanced processability, including funded research into thermoelectric fabrics. Composites of polymers with carbon nanotubes have also been a focus.

- O Fenwick, E Orgiu, Non-conventional charge transport in organic semiconductors: magnetoresistance and thermoelectricity, Molecular Systems Design & Engineering, 2, 47-56 (2017)
- LM Cowen, J Atoyo, MJ Carnie, D Baran, BC Schroeder, Organic Materials for Thermoelectric Energy Generation, , ECS Journal of Solid State Science and Technology, 6, N3080-N3088, (2017)
- P Taroni Jr, I Hoces, N Stingelin, M Heeney, E Bilotti, Thermoelectric Materials: A Brief Historical Survey from Metal Junctions and Inorganic Semiconductors to Organic Polymers, Israel Journal of Chemistry, 54, 534–552, (2014)
- M Baxendale, KG Lim, GAJ Amaratunga, Thermoelectric power of aligned and randomly oriented carbon nanotubes, Physical Review B, 61, 2705-2709, (2000)

8.2.22 University of Reading – Prof. Anthony Powell, Dr Paz Vaqueiro and Dr Ricardo Grau-Crespo

Thermoelectrics research at the University of Reading seeks to develop new materials containing earth-abundant elements. Research capabilities include materials synthesis and processing, structural characterisation, physical property measurements, calculation of band structures and modelling of key thermoelectric properties. Chemical substitution in skutterudite frameworks, coupled with the introduction of multiple fillers, is used to create high-performance (ZT > 1) materials for automotive applications.

Low-dimensionality is a key strategy in the design of sulphides and oxy-chalcogenides for energy recovery from low-grade waste heat. Intercalation into layered materials offers a means of tuning the balance between electronic and thermal transport, whilst rattling vibrations of weakly-bonded copper atoms in 2-D oxy-chalcogenides BiCuQO (Q = S, Se, Te) result in exceptionally low thermal conductivities. A range of sulphide-based materials, particularly those derived from minerals such as shandite ($Co_3Sn_2S_2$), bornite (Cu_5FeS_4) and tetrahedrite ($Cu_{12}Sb_4S_{13}$), is also under investigation: ball-milling providing an effective means of scaling up production.

- J Corps, P Vaqueiro, A Aziz, R Grau-Crespo, W Kocklemann, JC Jumas, AV Powell, Interplay of metal-atom ordering, Fermi level tuning and thermoelectric properties in cobalt shandites $Co_3M_2S_2$ (M = Sn, In), Chemistry of Materials, 27, 3946–3956, (2015)
- P. Vaqueiro, G. Guélou, A. Kalztoglou, R.I. Smith, T. Barbier, E. Guilmeau and A.V. Powell, The Influence of Mobile Copper Ions on the Glass-Like Thermal Conductivity of Copper-Rich Tetrahedrites, Chemistry of Materials, 29, 4080-4090, (2017)
- J Prado-Gonjal, P Vaqueiro, C Nuttall, R Potter, AV Powell, Enhancing the thermoelectric properties of single and double filled p-type skutterudites synthesized by an up-scaled ball-milling process, Journal of Alloys and Compounds, 695, 3598–3604, (2017)

8.2.23 Royal Holloway, University of London - Prof. Jon Goff

We have used central facility experiments combined with first-principles density-functional calculations to develop a deeper understanding of the physical properties of new thermoelectric materials. The observation of rattling modes using inelastic neutron and X-ray scattering provided a quantitative understanding of the suppression of the thermal conductivity in sodium cobaltate. The role of patterning was explored using neutron diffraction by doping sodium cobaltate with calcium, and the optimum thermoelectric properties were correlated with the formation of a particular superstructure. The suppression of transverse phonons by liquid-like diffusion in superionic conductors has been proposed as a means to dramatically reduce thermal

conductivity in thermoelectric materials. We have measured the ion transport and lattice dynamics in the original phonon-liquid electron-crystal copper selenide using neutron spectroscopy. We have shown that hopping time scales are too slow to significantly affect lattice vibrations and that the transverse phonons persist at all temperatures.

- DJ Voneshen, K Refson, E Borissenko, M Krisch, A Bosak, A Piovano, E Cemal, M Enderle, MJ Gutmann, M Hoesch, M Roger, L Gannon, AT Boothroyd, U Uthayakumar, DG Porter, JP Goff JP, Suppression of thermal conductivity by rattling modes in thermoelectric sodium cobaltate, Nature Materials, 12, 1028–1032, (2013)
- DG Porter, M Roger, MJ Gutmann, S Uthayakumar, D Prabhakaran, AT Boothroyd, MS Pandiyan, JP Goff, Divacancy superstructures in thermoelectric calcium-doped sodium cobaltate, Physical Review B, 90, 054101, (2014)
- DJ Voneshen, HC Walker, K Refson, JP Goff, Hopping time scales and the phonon-liquid electron-crystal picture in thermoelectric copper selenide, Physical Review Letters, 118, 145901, (2017)

8.2.24 University of Sheffield – Prof. Derek Sinclair

The Functional Materials and Devices group in the School of Materials Engineering investigate the structure-composition-property relationships of a wide range of electro-ceramics including thermoelectric oxides. Our current focus in these materials is to develop n-type ceramic oxides, predominantly based on reduced and rare-earth (RE) doped titanate perovskites and related phases. High electrical conductivity is induced by partial reduction of Ti^{4+} (d^o) to Ti^{3+} (d^1) ions by a combination of processing under reducing conditions (eg 5 % H_2 at > 1400 ^{o}C) and A-site deficiency by RE-doping, both of which facilitate oxygen-loss. The A-site deficiency is also effective in reducing the thermal conductivity and La-doped, A-site deficient $SrTiO_{3-d}$ ceramics can achieve ZT = 0.41 (at 973 K), Current efforts are to develop novel n-type materials by processing in air as opposed to using reducing conditions.

- Z Lu, DC Sinclair, IM Reaney, The influence of La-doping and heterogeneity on the thermoelectric properties of $Sr_3Ti_2O_7$ ceramics, Journal of American Ceramic Society, 99, 515-522 (2016)
- Z Lu, H Zhang, W Lei, DC Sinclair, IM Reaney, High-Figure-of-Merit Thermoelectric La-Doped A-Site-Deficient $SrTiO_3$ Ceramics, Chemistry of Materials, 28, 925–93, (2016)
- R Boston, WL Schmidt, GD Lewin, AC Iyasara, Z Lu, H Zhang, DC Sinclair, IM Reaney, Protocols for the Fabrication, characterization, and optimization of n-type thermoelectric ceramic oxides, Chemistry of Materials, 29 265-280, (2017)

8.2.25 Sheffield Hallam University – Dr Sima Aminorroaya Yamini

Thermoelectric research at Sheffield Hallam University aims to enhance thermoelectric performance of nanostructured bulk composite materials based on engineering chemistry, nanostructure and ratio of constituents. We also attempt to develop thermally stable diffusion barriers between thermoelectric materials and conducting electrodes for thermoelectric modules. Our current research has focused on developing chalcogenide (AQ, A = Pb, Ge, Sn and Q = Te, Se, S) and Mg_2Q (Q = Si, Ge, Sn) thermoelectric materials. A high thermoelectric efficiency of (ZT ~ 2) over a wide temperature range is achieved in the heavily-doped multiphase quaternary $(PbTe)_{0.65}(PbS)_{0.25}(PbSe)_{0.1}$ compounds through the composition modulation doping mechanism resulting from heterogeneous distribution of the dopant between precipitates and the matrix at elevated temperatures.

- R Santos, M Nancarrow, SX Dou, S Aminorroaya, Thermoelectric performance of n-type Mg_2Ge, Scientific Reports, 7, 3988, (2017)
- S Aminorroaya, T Li, D Mitchell, J Cairney, Elemental distribution within multiphase quaternary Pb chalcogenide thermoelectric materials determined using three-dimensional atom probe tomography, Nano Energy, 26, 157-163, (2016)

- S Aminorroaya, D Mitchell, Z Gibbs, R Santos, V Patterson, S Li, Y Pei, S.X Dou, G J. Snyder, Heterogeneous distribution of sodium for high thermoelectric performance of multiphase lead chalcogenides, Advanced Energy Materials, 5, 1501047, (2015)

8.2.26 University of Southampton - Dr Iris Nandhakumar

Research in the Nandhakumar group on thermoelectric materials focuses on utilising novel approaches for nanostructuring thermoelectric materials which include soft-templating via lyotropic liquid crystalline phases of polyoxyethylene surfactants and inverse lipid cubic phases. Materials prepared by this method are characterised by ordered networks of mesopores and uniform nano-architectures to lower κ whilst maintaining a high σ. Our approach to nanostructuring using soft templates has a number of distinct advantages over other approaches such as hot pressing or spark plasma sintering techniques of nanosized particles in that it allows very precise control of the resulting nanostructure of the electrodeposited material as the size and geometry of the template can be tuned by varying composition and experimental condition. We have also developed the use of ion-track etch lithography in combination with electrodeposition for fabricating high-density nanowire arrays of thermoelectric materials as well as devising innovative electrodeposition approaches for the formation of thick layers of thermoelectric materials.

- MR Burton, SJ Richardson, PA Staniec, NJ Terrill, JM Elliott, AM Squires, NM White, IS Nandhakumar, A novel route to nanostructured bismuth telluride films by electrodeposition, Electrochemistry Communications, 76, 71-74, (2017)
- C Lei, M Burton, IS Nandhakumar, Facile production of bismuth telluride thick layers in the presence of poly vinyl alcohol, Physical Chemistry Chemical Physics, 18, 1416414167, (2016)
- E Koukharenko, NWhite, X Li, I Nandhakumar, Ion-Track Etched Templates for the High Density Growth of Nanowires of Bismuth Telluride and Bismuth Antimony Telluride by Electrodeposition, ECS Transactions, 64, 9-14, (2015)

8.2.27 University of Southampton – Profs K de Groot, A. Hector, G. Reid, and P Bartlett

In thermoelectric devices, the reduction in phonon-mediated thermal conductivity and modification of the electronic density-of-states means that as the diameter of thermoelectric nanowires decreases below 10 nm, the thermoelectric Figure-of-Merit will continuously increase. This is the transformative breakthrough required to drive thermoelectric generators into new and much larger markets for energy harvesting and cooling applications.

We believe that we can overcome the fabrication limitations at the nanoscale that currently hold back Bi_2Te_3-based thermoelectrics by developing new forms of chemical vapour deposition and electrodeposition, the latter based upon weakly-coordinating solvents, which combines advantages innate to all forms of electrodeposition with a new level of material quality and control possible only in weakly-coordinating solvents.

- PN Bartlett, DA Cook, MW George, AL Hector, J Ke, W Levason, G Reid, DC Smith, W Zhang, Electrodeposition from supercritical fluids, Physical Chemistry Chemical Physics, 16, 9202-9219 (2014)
- PN Bartlett, SL Benjamin, CH de Groot, AL Hector, R Huang, A Jolleys, GP Kissling, W Levason, SJ Pearce, G Reid, Y Wang, Non-aqueous electrodeposition of functional semiconducting metal chalcogenides: $Ge_2Sb_2Te_5$ phase change memory, Materials Horizons, 2, 420-426, (2015)
- R Huang, SL Benjamin, C Gurnani, Y Wang, AL Hector, W Levason, G Reid, CH de Groot, Nanoscale arrays of antimony telluride single crystals by selective chemical vapor deposition, Scientific reports, 6, 27593, (2016)

8.2.28 University of Surrey – Prof. R Dorey

There is research into printing/digital printing of thermoelectric thick film (1-100μm) structures using a range of print techniques including ink jet and screen printing, large area spray deposition and micromoulding techniques. The activity ranges from synthesis of inorganic TE materials – both traditional Te-based as well as novel oxide and sulphide materials – through ink formulation and development of low temperature processing routes to achieving high quality film structures. This latter part is exploring techniques such as IR-flash sintering and laser sintering alongside conventional thermal treatments. Such treatments are designed to maximise the thermoelectric performances while minimising the potential degradation mechanisms including oxidation and TE-substrate interactions. By controlling the atmosphere and delivery of thermal energy it has been shown to be possible to integrate TE materials with a range of substrates including polyimide, glass and alumina. Work is also exploring the long-term stability of such systems where differences in microstructure, compared to traditionally fabricated devices, could lead to changes in degradation mechanisms.

- RA Dorey, Integrated Powder-based Thick Films for Thermoelectric, Pyroelectric and Piezoelectric Energy Harvesting Devices, IEEE sensors journal, 14, 2177-2184, (2014)
- EM Jakubczyk, CL Sansom, RA Dorey, The Role of Sodium-Rich Pretreatments in the Enhanced Sintering of Sodium Cobalt Oxide Thermoelectric Ceramics, Proceedings of the 11th European Conference on Thermoelectrics, Noordwijk, Netherlands, 37-42, (2014)
- RA Dorey, SA Rocks, F Dauchy, D Wang, F Bortolani, E Hugo, Integrating functional ceramics into microsystems, Journal of the European Ceramic Society, 28, 1397-1403, (2008)

8.2.29 SciTech Daresbury Campus, SuperSTEM Laboratory, Drs D.M. Kepaptsoglou and Q.M. Ramasse

The SuperSTEM Laboratory has developed a strong research programme on thermoelectric (TE) materials; firstly, in TE oxides in close collaboration with Prof. R. Freer (Univ. of Manchester) and Prof. S. Parker (Univ. of Bath). Secondly, in Heusler alloys and chalcogenide based TE systems, in collaboration with Dr. V.K. Lazavov (Univ. of York). Studies make use of the ability of high-energy-resolution, high-spatial-resolution scanning transmission electron microscopy and electron energy loss spectroscopy to provide highly accurate information on the crystal and chemical structure of promising TE materials, as well as to interrogate the materials' electronic structure at the atomic level. This characterisation then informs theoretical predictions from DFT electronic structure calculations combined with transport property calculations, with a view to link atomic-scale structure to macroscopic TE properties and performance. This highly symbiotic approach resulted in one of the most complete studies to date of the structure and electronic properties of the misfit-layered bismuth strontium cobaltate, as well as of Sr-Mo substituted $CaMnO_3$. New light was also shed on the doping mechanisms of chalcogenide-based thin film systems.

- JD Baran, M Molinari, N Kulwongwit, F Azough, R Freer, DM Kepaptsoglou, QM Ramasse, SC Parker, Role of Structure- and Defect Chemistry in High-Performance Thermoelectric Bismuth Strontium Cobalt Oxides, Chemistry of Materials, 28, 7470-7478, (2016)
- D Srivastava, F Azough, R Freer, E Combe, R Funahashi, DM Kepaptsoglou, QM Ramasse, M Molinari, SR Yeandel, JD Baran, SC Parker, Crystal structure and thermoelectric properties of Sr–Mo substituted $CaMnO_3$: a combined experimental and computational study, Journal of Materials Chemistry C, 3, 12245-12259 (2015)
- A Ghasemi, D Kepaptsoglou, AI Figueroa, GA Naydenov, PJ Hasnip, MIJ Probert, Q Ramasse, G van der Laan, T Hesjedal, VK Lazarov, Experimental and density functional study of Mn doped Bi_2Te_3 topological insulator, APL Materials, 4, 126103, (2016)

8.2.30 University of Swansea – Dr Matt Carnie

The main purpose of the thermoelectric research group at SPECIFIC-IKC, Swansea University is to deliver building scale energy generation and storage technologies to enable buildings to store, generate, and release their own energy. Specializing in hybrid-organic photovoltaic technologies, Dr Carnie has recently begun investigating the possibilities for thin film and printed thermoelectrics to enable thermal energy harvesting from the built environment.

- LM Cowen, J Atoyo, MJ Carnie, D Baran, BC Schroeder, Organic Materials for Thermoelectric Energy Generation, ECS Journal of Solid State Science and Technology, 6, N3080-N3088, (2017)

8.2.31 University of Warwick - Dr Neophytous Neophytou

The group focuses on theoretical simulations of electronic, thermal, and thermoelectric transport in nanostructured and low-dimensional materials and devices. His work on thermoelectrics is to develop advanced simulators that would address electrothermal transport in nanostructures by employing quantum transport and atomistic techniques. The group is currently involved in exploring nanomaterial designs that not only provide reductions in thermal conductivity but also provide large power factor improvements compared to their bulk counterparts. Ongoing collaborations with the groups of Prof. Dario Narducci (Milano-Bicocca), Prof. Giovanni Pennelli (Pisa), Prof. Marisol Gonzalez (Madrid), Prof. Nick Bennett (Heriot-Watt), test theoretical ideas and contribute towards demonstrating material prototypes. Collaborations with the Institute for Microelectronics at the Technical University of Vienna are providing the opportunity for large scale, high-performance simulator development.

- N Neophytou, X Zianni, H Kosina, S Frabboni, B Lorenzi, D Narducci, Simultaneous increase in electrical conductivity and Seebeck coefficient in highly Boron-doped nanocrystalline Si, Nanotechnology, 24, 205402, (2013)
- M Thesberg, H Kosina, N Neophytou, On the effectiveness of the thermoelectric energy filtering mechanism in low-dimensional superlattices and nano-composites, Journal of Applied Physics, 120, 234302, (2016)
- N Neophytou, H Kosina, Effects of confinement and orientation on the thermoelectric power factor of silicon nanowires, Physical Review B, 83, 245305, (2011)

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Appendix A

Activities in Thermoelectrics outside the UK

There has been significant activity in thermoelectrics in mainland Europe for the past thirty years. The establishment of the European Thermoelectrics Society (ETS) in 1995 provided a focus for work in the field and hosts an annual meeting. The annual International Thermoelectric Conference rotates annually between Europe, North America and Asia. To complement the summary of thermoelectric activity in the UK in the present document, this appendix includes two examples of graphical summaries compiled on behalf of: (i) the French Thermoelectric Society (Figure 14), showing active laboratories in France (2011-2014), and (ii) ETS (Figure 15) showing national societies, groups publishing papers on thermoelectrics (2007-2014), and groups involved in FP7 funded programs in thermoelectrics. Figure 16 identifies International Thermoelectric Society members and AAT members worldwide.
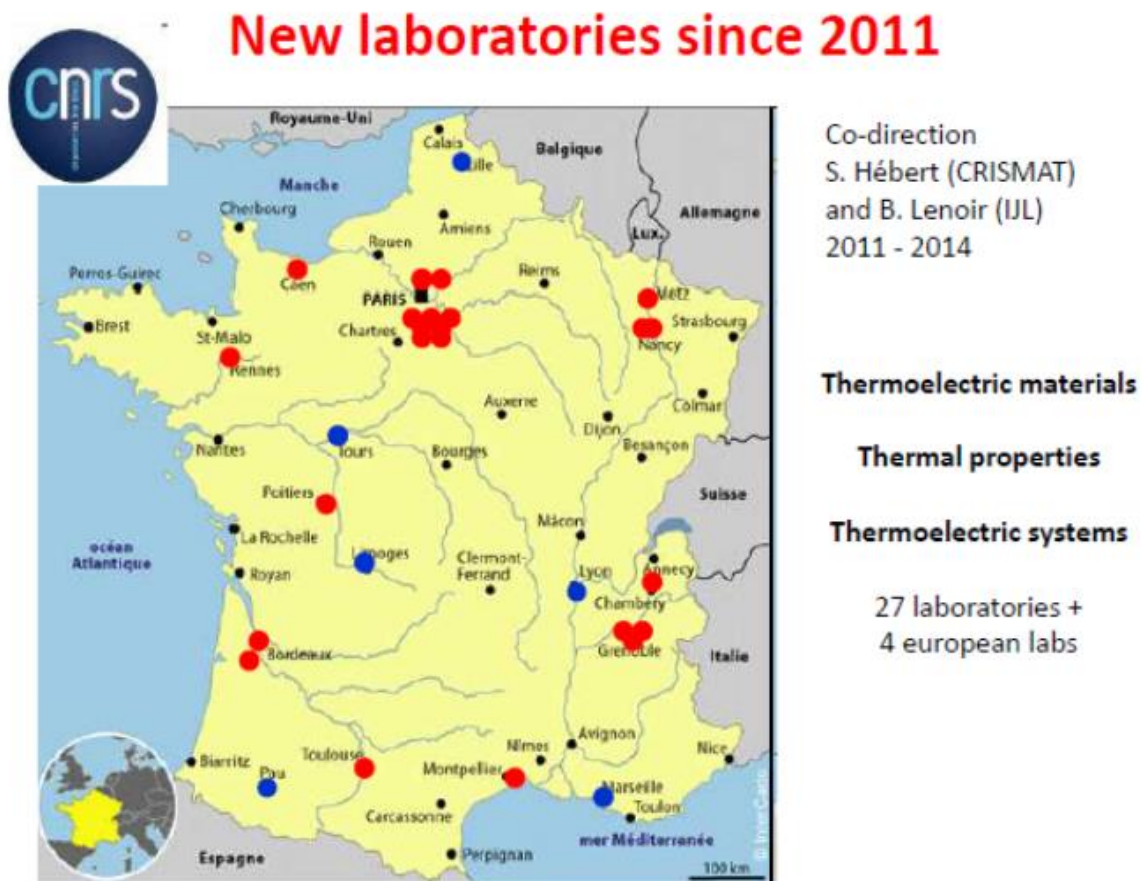

Figure 14 Thermoelectric laboratories in France (2011-2014)

Figure 15 Summary of European activities in the field of thermoelectricity (2014)

Figure 16 Thermoelectric worldwide

Appendix B

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