3rd Iberian Thermoeletric Workshop

ITW-2023

Campus Tecnológico e Nuclear of IST-UL
Lisboa, Portugal, 30-31 March 2023

Book of Abstracts

Editors:
Francisco P. Brito
António Pereira Gonçalves
Elsa Branco Lopes

Foreword

We are excited to make available the Book of Abstracts of the oral and poster presentations made at the third edition of the **Iberian Thermoeletric Workshop (ITW-2023)**.

The conference was hosted at Campus Tecnológico e Nuclear of IST-UL, Lisbon, Portugal, between March 30th and the 31st, 2023 and chaired by António P. Gonçalves (IST, C2TN).

The ITW meeting occurs every two years, alternating between Portugal and Spain. It aims to provide opportunities to improve the collaboration between researchers and specialists in the thermoelectricity field and also allow an open discussion about the most recent advances on materials, properties measurement, module fabrication, and device applications, with exchange of ideas, experiences, opinions and discussion about the most recent trends and priorities in this exciting topic.

This Book of Abstracts is published exclusively as a digital document containing a DOI (Digital Object Indentifier see below) for persistent online availability and referencing. The Editors of this Book of Abstracts were Francisco P. Brito (University of Minho,MEtRICs / Mechanical Eng. Department), António P. Gonçalves (IST, C2TN) and Elsa Branco Lopes (IST, C2TN), who also formed the local organizing committee of the conference. All submissions were approved after a peer review process.

The Official Workshop site can be found here.

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Lisbon, March 30th, 2023

The Editors,

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ITW 2023 Program

		March 30		March 31
9:15			Materials & Processing Theory and Modelling (MT)	**I.02** - Maria Ibañez
9:45				***MT.01*** - Viviana Sousa
10:00				***MT.02*** - Pablo Cerviño Solana
10:15				***MT.03*** - Norbert Marcel Nemes
10:30				***MT.04*** - José Javier Plata Ramos
10:45				***Coffee Break***
11:05			Materials & Processing (MP)	**I.03** - Sergi Riera Galindo
11:35				***MP.01*** - Clara Gomez
11:50				***MP.02*** - Mario Culebras Rubio
12:05				***MP.03*** - Javier Gainza Martín
12:20				***MP.04*** - Federico Miguel Serrano Sanchez
12:35				***Lunch+Posters***
14:15		**Registration**	Materials & Processing Theory and Modelling (MT)	**I.04** - Jose Antonio Alonso
14:45				***MT.05*** - Marta Maria González Barrios
15:00		***Welcome***		***MT.06*** - Duarte Moço
15:15	Other Topics (OT)	***I.01*** - Jorge Garcia Cañadas		***MT.07*** - Antonio M. Márquez
15:30				***MT.08*** - Diogo Lopes
15:45		***OT.01*** - Óscar Juan Dura		***Coffee Break***
16:00		***OT.02*** - Sergio Castro Ruiz	Devices &	**I.05** - Nuno Ferreira
16:15		***OT.03*** - Rodrigo Coelho		
16:30		***Coffee Break***		***DA.06*** - Ana Pires
16:50	Devices & Applications (DA)	***DA.01*** - Olga Caballero		***DA.07*** - André Pereira
17:05		***DA.02*** - Catarina Bianchi		***DA.08*** - Patricia Alegría
17:20		***DA.03*** - Marc Salleras		***DA.09*** - Lorenzo Pimpolari
17:35		***DA.04*** - Álvaro Casí		***DA.10*** - Leyre Catalán Ros
17:50		***DA.05*** - Irantzu Erro Iturralde		***Closing Session***
20:00		***Workshop Dinner***		

Thursday, March 30, 2023		
15:00 – 15:15	***Welcome Address***	
15:15 – 16:30	**Other Topics**	
	Session Chair: *António Pereira Gonçalves*	
15:15 – 15:45	**I.01**	Influencing the thermoelectric properties of materials using redox electrolytes, *Jorge Garcia Cañadas*
15:45 – 16:00	***OT.01***	Soft thermoelectricity based on hybrid gels, *Óscar Juan Dura*
16:00 – 16:15	***OT.02***	A Cr complex solution able to produce a 2.5 times power factor improvement in a nanostructured and porous Sb:SnO_2 film, *Sergio Castro Ruiz*
16:15 – 16:30	***OT.03***	Protective coatings for $Cu_{10.5}Ni_{1.5}Sb_4S_{13}$ tetrahedrites, *Rodrigo Coelho*
16:30 – 16:50	***Coffee Break***	
16:50 – 18:05	**Devices & Applications**	
	Session Chair: *Francisco Brito*	
16:50 – 17:05	***DA.01***	Flexible nanostructured thermoelectric devices grown inside polyester templates, *Olga Caballero*
17:05 – 17:20	***DA.02***	Transparent photothermoelectric thin film devices, *Catarina Bianchi*
17:20 – 17:35	***DA.03***	Power enhanced all-Si based micro-thermoelectric generators with integrated heat sink, *Marc Salleras*
17:35 – 17:50	***DA.04***	Thermoelectric subcooling system to improve the performance of vapour compression refrigeration systems, *Álvaro Casí*
17:50 – 18:05	***DA.05***	Optimization of a thermoelectric heat pump system for heating, *Irantzu Erro Iturralde*
20:00	***Workshop Dinner***	

Friday, March 31, 2023		
9:15 – 10:45	**Materials & Processing / Theory and Modelling**	
	Session Chair: *Óscar Juan Dura*	
9:15 – 9:45	***I.02***	Sintering solution processed nanoparticles: a way to tune microstructure through surface chemistry, *Maria Ibáñez*
9:45 – 10:00	***MT.01***	Screen-printing of thin film TEGs from PbSe quantum dots, *Viviana Sousa*
10:00 – 10:15	***MT.02***	Nanostructured bismuth telluride thin films grown by electrochemical deposition, *Pablo Cerviño Solana*
10:15 – 10:30	***MT.03***	Structural evolution and nanostructure of thermoelectric materials, *Norbert Marcel Nemes*
10:30 – 10:45	***MT.04***	High-throughput optimization of the thermoelectric efficiency of chalcogenides through nano-structuring: ab-initio calculations, machine learning and more, *José Javier Plata Ramos*
10:45 – 11:05	***Coffee Break***	
11:05 – 12:35	**Materials & Processing**	
	Session Chair: *Elsa Branco Lopes*	
11:05 – 11:35	***I.03***	Doping strategies to improve organic thermoelectric performance, *Sergi Riera-Galindo*
11:35 – 11:50	***MP.01***	Textile-based wearable TEG by electrochemical coating of felt fibers with conductive polymers, *Clara Gomez*
11:50 – 12:05	***MP.02***	Thermoelectric properties of layered nanocomposites based on conducting polymers, *Mario Culebras Rubio*
12:05 – 12:20	***MP.03***	Unexpected abrupt bond lengthening in GeTe as the origin of the anomaly in the experimental Seebeck coefficient, *Javier Gainza Martín*
12:20 – 12:35	***MP.04***	Investigation of the low-temperature thermoelectric transport and intrinsic electronic structure of half-Heusler TiCoSb, *Federico Miguel Serrano Sanchez*
12:35 – 14:15	***Lunch+Posters***	

Friday, March 31, 2023		
14:15 – 15:45	**Materials & Processing / Theory and Modelling**	
	Session Chair: *André Pereira*	
14:15 – 14:45	***I.04***	High-pressure synthesis of thermoelectric materials, *Jose Antonio Alonso*
14:45 – 15:00	***MT.05***	Microwave-assisted synthesis of thermoelectric chalcogenides, *Marta María González Barrios*
15:00 – 15:15	***MT.06***	Co-doping tetrahedrite: impact of Nickel and Selenium in thermoelectric properties, *Duarte Moço*
15:15 – 15:30	***MT.07***	Physical insights on the chemical factors that influence the thermoelectric properties in Cu- and Ag- based sulvanite, *Antonio M. Márquez*
15:30 – 15:45	***MT.08***	$SrTiO_3$ – based thermoelectrics prepared by Laser Floating Zone technique, *Diogo Lopes*
15:45 – 16:00	***Coffee Break***	
16:00 – 17:50	**Devices & Applications**	
	Session Chair: *Olga Caballero*	
16:00 – 16:30	***I.05***	Advancements in Laser Floating Zone processing for optimizing the thermoelectric properties of oxide materials, *Nuno Ferreira*
16:30 – 16:45	***DA.06***	The impact of collectors/absorbers on the efficiency of photo-thermoelectric devices, *Ana Pires*
16:45 – 17:00	***DA.07***	Wireless energy transfer using printable devices based on thermoelectricity: from concept to application, *André Pereira*
17:00 – 17:15	***DA.08***	Field operation and modelling of thermoelectric generators for high enthalpy geothermal anomalies, *Patricia Alegría*
17:15 – 17:30	***DA.09***	Flexible carbon-based thermoelectric generator with a phase change material for cold-chain monitoring, *Lorenzo Pimpolari*
17:30 – 17:45	***DA.10***	Prospects of volcano surveillance powered by thermoelectric generators: the Antarctica challenge, *Leyre Catalán Ros*
17:45 – 18:00	***Closing Session***	

Posters

Friday, March 31, 2023, 12:35 – 14:15	
P.01	Implementation of arrays of thermoelectric generators for nanosatellites: evaluation under atmospheric and space conditions, *Rui Costa*
P.02	On the thermal conductivity of thermoelectric polymers upon doping, *Jiali Guo*
P.03	Impedance spectroscopy: an excellent tool to fully characterize a thermoelectric device, *Jorge García Cañadas*
P.04	PDADMA-based solid electrolytes to significantly enhance the power factor of a thermoelectric oxide film, *Mauricio Solís de la Fuente*
P.05	Characterization of a possible thermoelectric material prepared from natural pyrite, *Vanina Gisela Franco*
P.06	Synthesis, optical band gap and thermoelectric properties of $Sr_{1+x}TiS_{3-y}$ chalcogenide perovskites, *Jinan Hussein Awadh Alshuhaib*
P.07	Maximizing exhaust heat utilization in light- and heavy-duty driving cycles through phase-change: Simulations and Experimental validation, *Rui Carvalho*
P.08	Soft Thermoelectric Materials: Design of 3D Printed Hydrogels, *Carlos Martin*

Influencing the thermoelectric properties of materials using redox electrolytes

Jorge García-Cañadas[1], Mauricio Solis-De La Fuente[1], Lourdes Márquez-García[1], Sergio Castro-Ruiz[1], Estelle Liautaud[2], Lucie Fournier[2], Camille Chatard[2], Pankaj Priyadarshi[3], Neophytous Neophytou[3]

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Low-grade heat (<200 ºC) is an abundant and ubiquitous source of energy widely available in our surroundings (e.g. body heat, heat from the sun, hot exhausts, industrial processes, etc.). The temperature dependency of the redox potential of electrolytes containing redox couples is employed in thermo-electrochemical cells to convert heat into electricity [1]. These devices are formed by two electrically conducting electrodes (usually Pt) separated by a redox electrolyte (e.g. 0.4 M aqueous ferro/ferricyanide). When the electrodes are under a temperature difference, an electrical voltage of a few mV/K can be achieved, and electrical current can be generated.

Here, we propose a new device for the conversion of heat into electricity. It consists of a film of an electrically conducting material (Pt, PEDOT:PSS, porous C or fluorine-doped SnO_2), contacted by metallic contacts at its ends, which is combined in parallel with a redox electrolyte (0.4 M aqueous ferro/ferricyanide). Under this configuration, an open-circuit voltage can be generated when a temperature gradient is established due to the temperature dependency of the redox electrolyte, and the electrical current can flow through both the electrolyte and the conducting materials. It was observed that the highest open-circuit voltages (Seebeck coefficients) were achieved when most of the current flows through the electrolyte. This new device can offer other benefits that will be discussed.

References

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Topic: Other Topics on Thermoelectricity (OT)
Oral Presentation *OT.01*

Soft Thermoelectricity based on hybrid gels

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Organic compounds are interesting for the thermoelectric conversion due to their abundance and sustainability, resulting in a cheap and versatile approach towards energy harvesting. In addition, they offer the possibility to design soft and flexible devices and also the ability to profit from non-conventional thermoelectrical effects such as the thermogalvanic effect [1], which we develop in this work. Through this effect, a temperature difference in an electrolyte produces the gradient of a redox couple which reacts at electrodes producing a charge difference and current.

Here focus is on electrolytes based on gels which offer advantages over conventional liquids related to their better stability and safety [2]. We employ a *Digital Light Processing* printer, settled to print hydrogels, which allows designing specific shapes and sizes offering a large versatility. We have prepared hydrogels with different functional groups to explore the ability to anchor different redox couples: $Fe^{3+/2+}$ and $Fe(CN)_6^{4-/3-}$. The influence of the couple concentration and swelling (water content) over the thermogalvanic behavior and the output power is systematically analyzed.

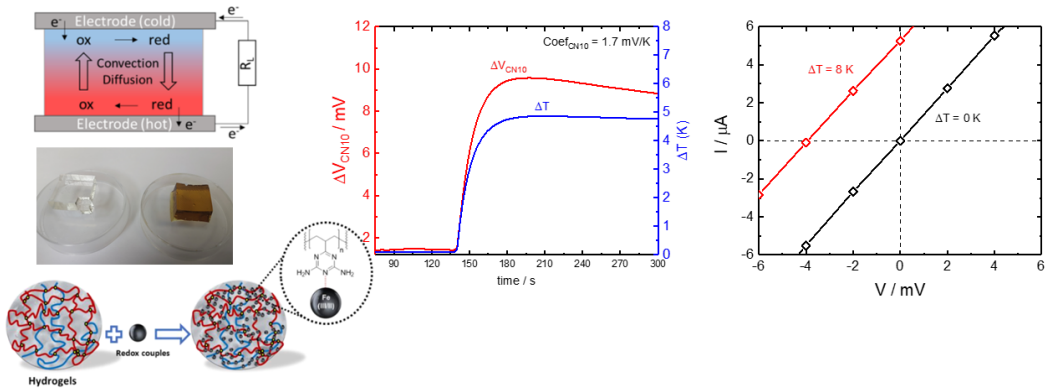

Fig. 1. (left) Schema of thermogalvanic effect [3] and blanc and doped $Fe^{3+/2+}$ complex hydrogels analyzed here. (center) Thermovoltage and temperature difference evolution through time. (right) current and voltage relation due to the temperature gradient.

References

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[3] Y. Zhang et al., *Nature Communiations* **12**, 5269 (2021).
[4] M. Massetti et al., *Chemical Reviews* **121**, 12465 (2021).

Topic: Other Topics on Thermoelectricity (OT)
Oral presentation *OT.02*

A Cr complex solution able to produce a more than 3 times power factor improvement in a nanostructured and porous Sb:SnO_2 film

Sergio Castro-Ruiz[1], Lourdes Márquez-García[1], Mauricio Solis-de la Fuente[1], Braulio Beltrán-Pitarch[1], Pablo Iñigo-Rabinal, Gregorio Guisado-Barrios[2], Jorge García-Cañadas[1]

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In the search of more efficient thermoelectric (TE) materials, significant improvements in *ZT* have been achieved, mainly due to the reduction of the thermal conductivity. In contrast, enhancements in the power factor $PF=\sigma S^2$, being σ the electrical conductivity and S the Seebeck coefficient, have been minor. Recently, large *PF* improvements have been shown in a novel solid-liquid TE system, consisting of a porous nanostructured TE solid (Sb-doped SnO_2) in contact with different electrolytes (salts in a liquid media) [1].

Here, we have investigated a new electrolyte for this system, a Cr (III) complex [chromium (III) acetylacetonate] dissolved in 3-methoxypropionitrile (3-MPN) in 0.1M concentration. Using this electrolyte in contact with the Sb-doped SnO_2 film, an average *PF* enhancement of 3.4 times was achieved. This was due to an average decrease of 23% and 83% in the absolute value of the Seebeck coefficient and the electrical resistivity of the solid, respectively. The possible mechanisms responsible for these changes are investigated and analysed. It was found that the current of the device can only flow through the solid film, and both the 3-MPN solvent and the Cr complex can induce an increase in the carrier concentration of the oxide.

References

[5] L. Márquez-García et al., *ACS Applied Energy Materials* **1**, 254 (2018).

Topic: Other Topics on Thermoelectricity (OT)
Oral presentation *OT.03*

Protective Coatings for Cu10.5Ni1.5Sb4S13 Tetrahedrites

Rodrigo Coelho[1], Elsa Branco Lopes[1], Francisco P. Brito [2], António Pereira Gonçalves[1]

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Abstract:

Facing the present world energy crisis due to its large dependency on fossil energies, it is more important than ever to transition towards renewable energy sources and systems, being fundamental for the society to implement new energy solutions that can be affordable, highly effective, and sustainable. In this context, thermoelectric (TE) materials can be seen as alternative solutions with great potential for energy conversion and recovery, since they are capable of converting heat to electricity, and vice-versa, using the Seebeck and Peltier effects, respectively. Such capacity allows TE materials to produce energy from waste heat without the need of moving parts, with low maintenance needs, and with zero gas emissions. At the same time, TE materials can present a high versatility, being capable of being shaped to solid state devices that can present multiple configurations and geometries, and to be used in a wide range of applications ranging from energy generation (waste heat recovery) up to remote sensing (sensors for the internet of things (IOT) and industry 4.0) [1,2]. Having in consideration that about 2/3 of all energy produced by mankind is lost mainly as waste heat [3], thermoelectric materials can be excellent tools, allowing us to become more sustainable by maximizing our energetic usage (reducing waste) and reducing our carbon footprint.

Despite their great potential, TE materials are not used in large scale, especially because most of the existing commercial devices contain rare and toxic elements such as tellurium, bismuth, and lead. The rarity of some elements, combined with a weak chain of supply and low efficiency (<12%)[4], make TE devices unattractive/difficult to implement in large scale [5]. To change this tendency, new TE materials are being studied and developed. Within a large variety of materials with potential for TE applications, the tetrahedrites (copper antimony sulfosalts) are seen as good candidates for replacing the Bi and Te based devices. These materials, have a $Cu_{12-x}M_xSb_4S_{13}$ general formula , with M = Mn, Zn, Co, Cd, Al, etc., and x ranging between 0 and 2 [6]. They crystallize in a complex cubic cell (I-43m), and are abundant and cheap (~6 €/Kg) [7]. At the same time, they usually present low toxicity and good thermoelectric properties (zT ~1 around 600 K) [6]. However, these materials oxidize and degrade easily when exposed to air at medium temperatures. Consequently they have to be protected or covered in order to keep their TE properties during operation [8].

In the present study, several coatings applied on Nickel doped tetrahedrites were tested. The covered tetrahedrite materials were submitted to 573 K during 300 h (~14 days) under air conditions. The effectiveness of the several coatings is discussed based on the analysis of the materials by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The identification of effective protective coatings and the identification of the main degradation/oxidation mechanisms are expected to allow the future development of a novel generation of thermoelectric devices capable of working during long periods at a reduced cost and therefore becoming more easily widespread.

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(2) dos Santos, A. D.; de Brito, S. C.; Martins, A. V.; Silva, F. F.; Morais, F. Thermoelectric Energy Harvesting on Rotation Machines for Wireless Sensor Network in Industry 4.0. *2021 14th IEEE Int. Conf. Ind. Appl. INDUSCON 2021 - Proc.* **2021**, 694–697. https://doi.org/10.1109/INDUSCON51756.2021.9529630.

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Topic: Devices & Applications (DA)
Oral presentation *DA.01*

Flexible nanostructured thermoelectric devices grown inside polyester templates

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We present the fabrication and first characterizations of nanostructured thermoelectric generators based on bismuth telluride (n-type semiconductor) and tellurium (p-type semiconductor). The main applications of such generators are to harvest body waste heat for powering wearable devices, and therefore the flexibility of the structure is mandatory to be able to adapt the generators to the human skin, along with a cost-effective and scalable fabrication method.

As it has been previously shown, the thermoelectric performance of such nanostructures should be enhanced when compared with thin films grown in similar conditions [1]. In this work, the nanostructures have been grown via electrochemical deposition inside nano-porous commercial polyester filters. The morphology, composition, crystal orientation, etc. have been characterized and optimized to obtain a high filling ratio of nanostructures oriented along the [110] direction with stoichiometric composition, given that these show the best properties when dealing with applications for the out-of-plane direction [2].

For the final thermoelectric generator, apart from the active thermoelectric material, top and bottom electrical contacts needed to be implemented [2]. In our case, those have been fabricated as follows: the bottom electrode used was an electron-beam evaporated gold layer, which was later thickened with a further electrochemical deposition of gold. Following the growth of the thermoelectric nanostructure, the metallic top electrode was fabricated with a nickel electrodeposited layer.

In order to optimize the geometry of the thermoelectric devices, COMSOL MULTIPHYSICS® simulations were carried out using the properties of the nanostructures measured experimentally. Finally, the first characterizations of the actual devices have been performed.

References

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Topic: Devices & Applications (DA)
Oral presentation *DA.02*

Transparent Photothermoelectric Thin Film Devices

C. Bianchi,[1] A.C. Marques[1], R.C. da Silva[2], T. Calmeiro[1] and I. Ferreira[1]

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One of the alternatives that have been explored as a heat source for thermoelectric devices and generate energy is solar energy, i.e. use light as a heat source [1].
Transparent thin film devices combining photovoltage and thermoelectric effects are still rare. These devices have high transmittance in the visible range and more than 50 % reflection or absorption in the near-infrared range.
The structure of the transparent photothermoelectric (PTE) thin film device consists of a glass on which a thermoelectric thin film (Aluminum Zinc Oxide) is deposited, and a reflector (transparent conductor oxide (TCO)-metal-TCO structure) or absorber layer (transparent semiconductor oxide (TSO)) is deposited in half of the sample.
When the sample is uniformly heated, a thermoelectric effect is observed and when irradiated, a photovoltage proportional to the radiation intensity is also observed. This photovoltage was continuously monitored on samples placed in a glass window facing south and throughout the day, the photovoltage varies from 0 to 300 µV proportionally to the light intensity.
A glass/window coated with a transparent thermoelectric thin film and a reflector layer, such as a low-e coating, can improve the energy efficiency of buildings and convert thermal and photonic energy into electrical energy.
Therefore, in this work, a new concept for capturing NIR radiation and converting it into voltage using thin film structures transparent to visible light has been demonstrated. This type of structure is particularly interesting for window glass applications.

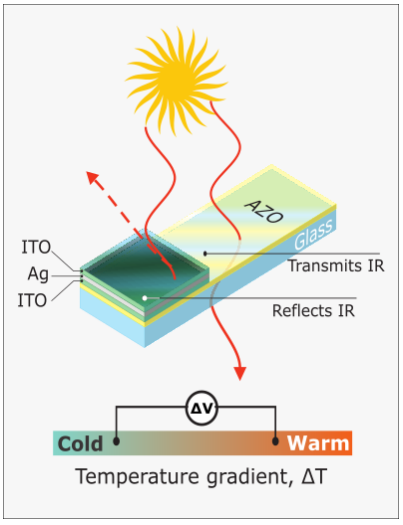

Fig. 1. Scheme of a transparent photothermoelectric thin film device [2].

References

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Topic: Devices & Applications (DA)
Oral presentation *DA.03*

Flexible carbon-based thermoelectric generator with a phase change material for cold-chain monitoring

Marc Salleras,[1] Lorenzo Pimpolari[1], Neus Sabaté[1], Joaquín Santander[1], Luis Fonseca[1]

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A realistic transition to renewable energy sources, such as solar, wind energy, etc., also requires a greater integration of differentiated energy harvesting and saving technologies [1]. In this context, thermoelectric power can play an important role, and be harnessed in several applications of practical interest [2]. Here, we propose an application for cold-chain monitoring of high value-added products that require to be preserved at controlled temperatures throughout the distribution chain. This is in fact a fundamental and ever-growing necessity in the industry of production and distribution of many essential goods, such as food and pharmacy products.
Specifically, we propose a sensor based on a thermoelectric generator (TEG) embedded in a flexible substrate the size of a credit card that can be applied directly to the product to be monitored (Fig. 1a). The working principle is based on the presence of a phase change material (PCM) on one side of the TEG, while the other is directly exposed to the surrounding environment (Fig. 1b). In this way, as long as the product is kept at a correct temperature, both sides of the generator are at the same temperature, and there is no thermoelectric power generation. On the other hand, if the product is exposed to an out of range temperature, one side of the TEG will rapidly evolve towards that temperature, while the other side will maintain the temperature of the phase change transition until the PCM has melted completely. This allows the creation of a transient temperature difference, resulting in the generation of an electrical voltage that can be detected by an external circuitry. The time evolution of this thermal transient provides information on the amount of energy exchanged with the environment, thus providing additional information than merely the exceeding of the maximum allowed temperature. To have practical utility, the whole sensor must be inexpensive and employ sustainable materials. For these reasons, we used paper as substrate because of its low cost, flexibility and recyclability [3]. For the fabrication of the thermoelements we have employed carbon-based materials because they are earth-abundant, compatible with deposition through low-cost, large-area printing and coating techniques, and have suitable mechanical and thermoelectric properties [4].
For the first prototypes, we printed all materials by blade coating using a K Printing Proofer. The p-type elements are deposited starting from a commercial carbon/graphite paste with the addition of wt1% single-walled carbon nanotubes to enhance its thermoelectric properties. For the n-type elements, we further added an n-type dopant (polyethylenimine, wt10%) to the previously described ink. The thermoelectric properties of the materials are obtained on samples with a single thermocouple. Figs. 1c, d show the square resistance and Seebeck coefficient of 5 different TEGs, measured over more than 100 days. As it can be observed (inset of Fig. 1c, d), the average square resistance and Seebeck coefficient are in the order of 7 Ω/□ and 60 µV/K. Moreover, the thermoelectric properties are found to be stable over the observed period, which is a crucial aspect for practical applications. As a first demonstrator, we fabricated a TEG on paper consisting of 12 thermoelements (inset of Fig. 2a), which has an internal resistance of around 700 Ω. Fig. 2a shows the open circuit voltage as a function of the temperature difference applied at the ends of the TEG. Finally, we carried out preliminary measurements on a single p-type thermoelement to evaluate the effect of the PCM. We employed a PCM material with a phase change temperature of 42 ºC. The open-circuit voltage (Fig. 2b) was initially measured by keeping the sample at room temperature, and then

introducing it into an oven preheated to 65 ºC under three different conditions: on the bare sample (gold curve), on the sample with a block of poly(methyl methacrylate) (PMMA3, mm thick) placed on one side (orange curve), and on the sample with a block of PMMA filled with the PCM placed on one side (black curve). While in the first case the voltage is negligible, in the other two cases there is a voltage peak due to the PMMA acting as a thermal insulator, unbalancing the thermal transient between the two sides of the thermoelement. However, the response in the presence of the PCM is different, showing a second peak attributed to the melting of the PCM material. The presence of the PCM generates a larger thermal transient that can be correlated to a sample exposure to an undesired temperature for a certain time. This represents an interesting proof of concept, although a detailed analysis becomes necessary to evaluate the dependence between amount of energy exchanged with the environment and the volume of the PCM, before extending this approach to an entire TEG for the application of interest.

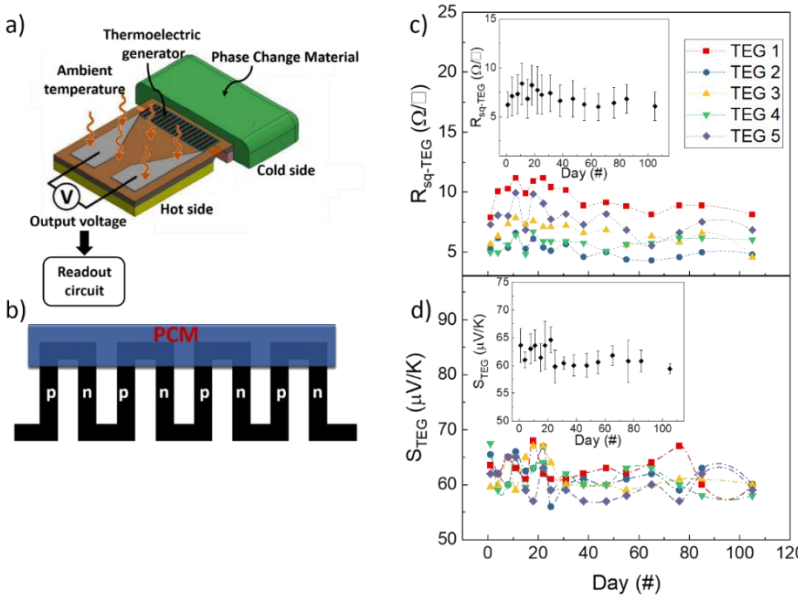

Fig. 1. Schematic representation of the device (a) and detail representing the structure of the TEG (b). Square resistance (c) and Seebeck coefficient (d) of 5 different thermocouples over more than 100 days. The insets show the respective mean values over time (the error bars are the standard deviation).

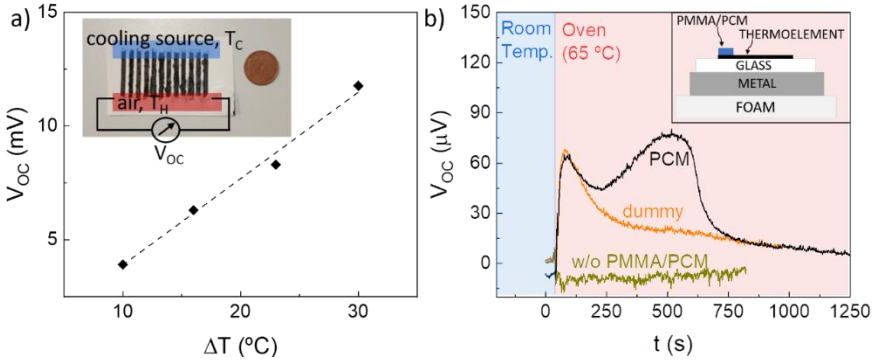

Fig. 2. (a) open circuit voltage of a TEG on paper as a function of the temperature difference. In the inset, a photograph of the TEG. (b) Evolution of the open circuit voltage of a single thermoelement initially measured at room temperature and then placed at 65 ºC under different measurement conditions: exposed (gold curve), covered with a dummy PMMA square (orange curve), and covered with a PMMA block filled with the PCM (black curve). In the inset, a schematic cross section of the device under measurement.

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Topic: Devices & Applications (DA)
Oral presentation *DA.04*

Thermoelectric subcooling system to improve the performance of vapour compression refrigeration systems

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The refrigeration sector plays an important role in confronting climate change, being responsible for 7.8 % of the global emissions and consuming 20 % of the electricity worldwide [1-2]. In addition, energy consumption of the sector is expected to double or triple by 2050 [3], which remarks the paramount importance of developing efficient and environmentally friendly refrigeration systems.

This work focuses on reducing the environmental impact of the refrigeration sector by the development of a Thermoelectric Subcooling System (TESC) that is able to boost the performance of environmentally friendly vapour compression cycles that use natural refrigerants such as CO_2 or NH_3. The main objective of the thermoelectric system is to efficiently subcool the refrigerant at the outlet of the gas-cooler/condenser in order to increase the cooling capacity of the refrigeration system and compensate the extra consumption of the system, so that the performance of the refrigeration system is enhanced. Through the development of an experimental test bench the thermoelectric subcooler in combination with an internal heat exchanger is able to boost the performance of the vapour compression refrigeration system by 22.5 % [4].

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Topic: Devices & Applications (DA)
Oral presentation *DA.05*

Optimization of a Thermoelectric Heat Pump System for Heating

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The current need to carry out an energy transition towards a 100 % renewable energy horizon places the energy storage as the key. Numerous researchers are studying an optimum method to enhance a reliable energy storage, where thermal energy storage presents a great potential [1]. In 2019, the first delocalized thermal energy storage (TES) installation based on electrical resistances was placed in Hamburg. In this case, electrical resistances were used to heat an airflow, which stored thermal energy together with crushed volcanic rocks in a deposit [2]. Electrical resistances used for energy conversion from electricity to heat stands out for its simplicity. However, the use of electrical resistances presents a limited energy conversion efficiency of one. The Coefficient of Operation (COP) is the value that relates the heat dissipated ($\dot{Q}_h$) to the hot reservoir to the consumed electric power ($\dot{W}_e$).
This work proposes the use of thermoelectric technology working as a heat pump to improve the load process of TES systems based on solid materials heated up by a hot airflow. This technology not only is able to achieve COP values greater than one, but also it is very easy to control, a scalable technology, with no moving parts and it does not need refrigerants. Therefore, three different thermoelectric heat pumps (TEHP) have been developed, built and experimentally tested to obtain an optimized thermoelectric system. The first configuration is the simple one, which is composed with a unique module. The second configuration is the direct multistage one, where two TEMs are located are thermally connected to each other. Finally, the third configuration is a two-stage TEHP configuration with a phase change intermediate heat exchanger (pc-intHX) with a relation of thermocouples between stages of two [3].
Experimental tests were carried out in a climate chamber at 25 °C to study the COP of the different configurations when heating an airflow of 15 m³/h. The obtained experimental results were analysed and used to computationally optimize a final configuration of TEHP system. The performance study showed that for low temperature differences between heat sinks, the simple TEHP presents a better performance than the multistage ones. However, when the temperature difference increases, the use of a multistage configuration is needed, where the multistage TEHP with pc-intHX obtains a better performance
Thanks to the experimental results, a configuration that combines the different TEHP configurations for a real application has been developed. The system presents three simple TEHP followed by three multistage TEHP with pc-intHX. An improvement of the COP between 18 - 44 % could be reached in the TES load procedure when the optimized TEHP system is included and to heat the airflow from 90 to 200 °C.
In conclusion, this work an optimal TEHP system to heat up an airflow used to thermally store energy and based on experimental results has been designed. This system is able to drastically improve the load process of a TES, reaching COP increments bigger than the 22 % in all the studied cases. Therefore, the great potential of thermoelectric technology in this kind of applications has been demonstrated.

Acknowledgement
We would like to acknowledge the support of the Government of Navarre funds under the grants PC066-067-068 FlexORCstorage

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Topic: Thermoelectric Materials & Processing / Theory and Modelling (MT)
Invited Oral Presentation *I.02*

Sintering solution processed nanoparticles: a way to tune microstructure through surface chemistry

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Nanoparticles can be used as tunable precursors to produce macroscopic solids with specific structural features by controlling the density and microstructure of the solids through the consolidation process. The consolidation process, such as hot pressing or spark plasma sintering, is preferred in order to provide the material with densities as close as possible to the respective theoretical density. The characteristics of the particles, such as size, shape, composition, and surface chemistry, determine the sintering process and therefore dictate densification, grain growth, and the final microstructure of the material. A nanoparticle can be considered as a multi-structured system consisting of an inorganic nanocrystalline domain, named the inorganic core, surrounded by surface species. Both the inorganic and surface species are tunable parameters in the design of nanoparticle-based precursors. The surface chemistry of the nanoparticles can be adjusted during sintering to achieve a solid with specific targeted features.

Two approaches to controlling the surface chemistry of the particles need to be separated. One refers to the particle termination atoms, the other to the connected adsorbates that can be covalently bonded molecules or electrostatically adsorbed ionic groups. The surface adsorbates, intentionally or unintentionally introduced, are critical to controlling densification, grain growth, and the final microstructure of the material. Herein, we will discuss the structural properties controlled through different surface species and discuss their effect on the electrical and thermal transport to evaluate their potential as thermoelectric materials.

Topic: Thermoelectric Materials & Processing / Theory and Modelling (MT)
Oral Presentation *MT.01*

Screen-printing of thin film TEGs from PbSe quantum dots

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Thin film thermoelectric generators (TEGs) afford an interesting opportunity for powering wearable electronics and internet-of-things. As the range of such applications continuously broadens, it is becoming important to develop less energy-demanding fabrication routes towards thin film TEGs [1]. Here, we propose screen-printing approach as an easy to scale-up and industry-relevant technology to fabricate thin film TEGs from PbSe quantum dots (QDs).
The PbSe QDs with spherical morphology and monodisperse size of 11 nm were successfully synthesized through colloidal heating-up method. Next, PbSe QD ink was formulated, and used for the fabrication of the thermoelectric (TE) thin films by means of screen-printing followed by annealing. Notably, the phase composition, size, and morphology of the PbSe QDs were maintained after annealing at 600 ºC. The annealing treatment is essential to remove organic matter from the screen-printed TE thin films, since carbon residues from QDs' capping ligand and ink binders can reduce charge carrier mobility within the resultant film [2].
Electrical properties, measured at room temperature by Hall effect, reveal that the as-fabricated PbSe QD thin films have a bulk carrier concentration of 3.8×10^{18} cm^{-3}, electron mobility of 7.9×10^{-1} cm^2 V^{-1} s^{-1} and electrical conductivity of 50 S m^{-1}. A maximum Seebeck coefficient of 561 µV K^{-1} was obtained at 143 ºC and a highest electrical conductivity of 123 S m^{-1} was reached at 197 °C. Positive Seebeck coefficient indicates *p*-type nature of the thin films [3].
Further, several TEG geometries were explored with screen-printed *p*-type PbSe QDs and *n*-type Ag commercial paste. TEGs performance with 6 pairs of PbSe/Ag legs was characterized using a custom-built setup which can accurately control the temperature gradients by 4 commercial TE modules. An Optris PI 450 infrared (IR) camera placed over the setup was used to acquire thermal images of the TEGs (Figure 1), and the obtained results will be presented and discussed.

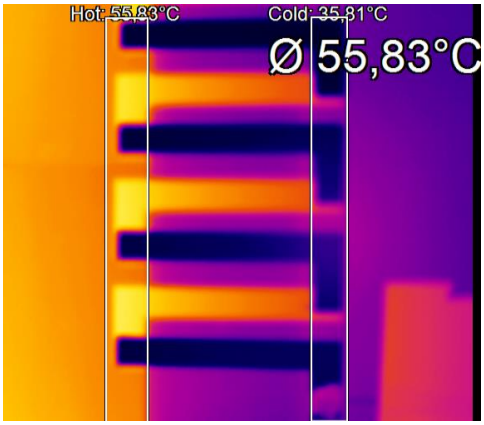

Fig. 1. Thermogram of 20 °C gradient within the screen-printed TEG with *p*-type PbSe and *n*-type Ag legs.

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Nanostructured bismuth telluride thin films grown by electrochemical deposition

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Electrochemical deposition is a scalable and widely used technique in the fabrication of nanostructured materials and is optimal for the fabrication of thermoelectric generators. In this work, bismuth telluride thin films have been grown using a three-electrode electrochemical cell, obtaining a nanometric structure without using any template, thus simplifying the fabrication process and reducing its cost.

This upgrade is achieved by adding sodium lignosulfonate [1, 2] into the electrochemical bath, and, as a result, we obtain stoichiometric thin films preferably oriented along the [110] direction and nanostructured in 12 nm thick nano-platelets. This kind of nanostructuration is expected to reduce the thermal conductivity, as it is the case in bismuth telluride electrodeposited nanowires [3] and 3D-nanowire networks [4]. Because the nano-platelets are interconnected, the thermoelectric effect is produced in two directions: in plane and out of plane, resulting in highly anisotropic films.

Our objective is to optimize the thermoelectric properties of these films, enhancing their figure of merit, *zT*. To do so, we studied the influence of the different fabrication parameters, such as the composition of the bath, the voltage applied, and the deposition time, on the final properties of the films. The films have been characterized obtaining promising *zT* values.

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Topic: Thermoelectric Materials & Processing / Theory and Modelling (MT)
Oral Presentation *MT.03*

Structural Evolution and Nanostructure of Thermoelectric Materials

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A good thermoelectric material must have a high Seebeck coefficient (S), be a good electrical conductor and a good thermal insulator. The efficiency of a thermoelectric is commonly characterized with its thermoelectric figure of merit, $zT=\sigma S^2T/\kappa$. Thermoelectrics could play an important role in saving energy in a future, sustainable, economy, if only they had a zT>4. Today, the best materials, commercial highly doped semiconductors, do not exceed by much zT ~ 1, while state-of-the-art zT reported very recently in materials such as SnSe or GeTe do not exceed zT ~ 2.5. The electrical (σ) and thermal (κ) conductivity in metals is tied by the Wiedemann-Franz law. However, κ also has an important contribution in semiconductors due to the vibrations of the crystal lattice (κ_{latt}). There are several strategies pursued to improve thermoelectric properties, including nanostructuring or the so-called "phonon glass, electric crystal" (PGEC) approach, aiming to decrease κ_{latt} in different ways, while preserving the good electronic properties (S and σ).

We use straight-forward arc-melting synthesis to obtain thermoelectric materials with promising properties. We characterize the static and dynamic structure with neutron scattering, with Rietveld refinement analysis to obtain both the crystalline structure and the dynamics of the constituent atoms through thermal factors (atomic displacement parameters).

We correlate this structure with the thermoelectric properties, in particular with the contribution of the crystalline network to the thermal conductivity in families of intermetallics: alloys of Bi_2Te_3 with Sb and Se, GeTe and its alloys, and PbTe and its alloys, and finally SnSe and its alloys, where we obtained the highest figure of merit (zT~1.8) to date in any n-type polycrystalline sample.

We also show how a simple analysis of the atomic displacement factors in terms of independent Einstein oscillators sometimes can yield surprisingly good approximations of the relevant phonon energies, when compared to inelastic neutron spectra and *ab-initio* calculations [1].

In this talk several examples of these material families will be described, always aiming to establish correlations between the structural peculiarities with the observed properties.

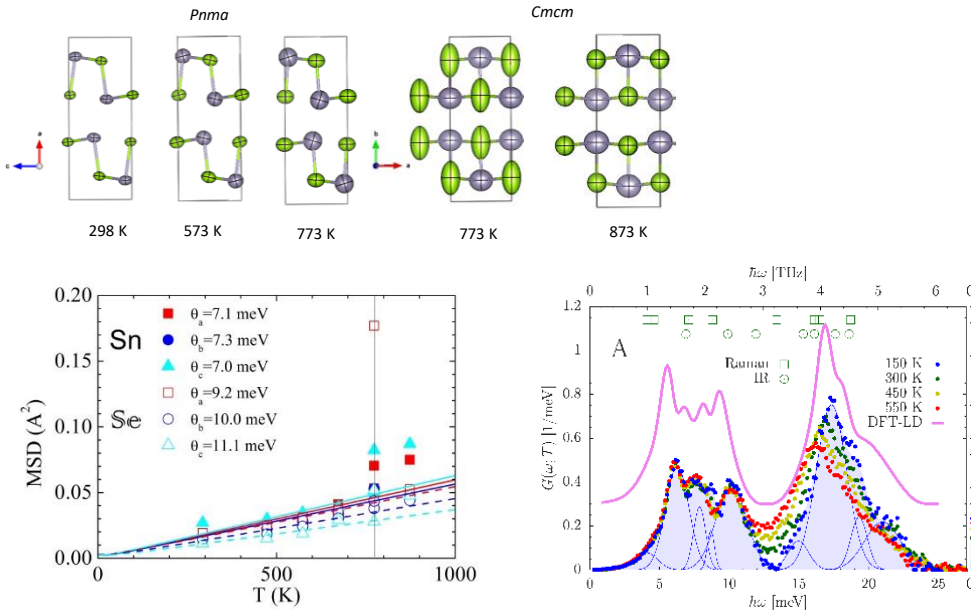

Figure 1. *SnSe: Structure as a function of temperature (top) from NDP, Einstein-oscillator analysis of the ADPs (bottom left), and inelastic neutron spectra (bottom right)*

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Topic: Thermoelectric Materials & Processing / Theory and Modelling (MT)
Oral Presentation *MT.04*

High-throughput optimization of the thermoelectric efficiency of chalcogenides through nano-structuring: ab-initio calculations, machine learning and more.

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The optimization of new and more efficient thermoelectric, TE, materials has been hindered by the interdependence of electronic and phonon transport properties and the multitude of variables that affect the thermoelectric figure of merit, *ZT*. Traditional approaches involving time-consuming and expensive synthesis and characterization processes are not practical for exploring large chemical spaces and optimizing properties that depend on numerous variables. This work employs a high-throughput framework that combines ab-initio calculations and machine learning to chart systematically and accurately the thermoelectric properties of chalcogenides [1,2]. In addition to examining the already well-established temperature dependence of *ZT*, the study investigates the effect of carrier concentration and polycrystalline average grain size on *ZT* (Fig. 1). By calculating the mean free paths of electrons and phonons, the study demonstrates the potential for automating and rationalizing the optimization of TE materials through nano-structuring [3]. The study finds that the difference in the mean free paths of electrons and phonons for different chalcogenides disentangles the connection between the power factor and lattice thermal conductivity when reducing the crystal size. The study predicts *ZT* values up to 2 for some p-type chalcogenides at 700 K when the average grain size is in the 10-100nm range. Furthermore, the *ZT* of some of the nanocrystalline samples are almost three times larger than that of single-crystal or micro-metric polycrystalline materials. The results demonstrate the potential of computational approaches in accelerating the discovery of thermoelectric materials.

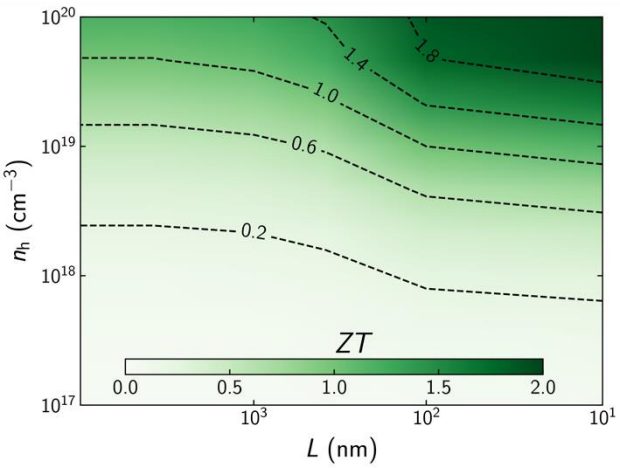

Fig. 1. Thermoelectric figure of merit, *ZT*, dependence on average grain size, *L*, and carrier concentration, *n*, at 700 K for a *p*-type chalcopyrite.

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Doping Strategies to Improve Organic Thermoelectric Performance

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Organic thermoelectric generators (OTEGs) are devices that use organic thermoelectric materials to convert heat directly into electricity. OTEGs offer several advantages over traditional inorganic thermoelectric generators, including their low thermal conductivity, flexibility, low cost, and easy processability. Doping of organic semiconductors with suitable dopants is a powerful tool to optimize their electrical conductivity and Seebeck coefficient.

In this context, the impact of singly occupied molecular orbital (SOMO) energy on the n-doping efficiency of benzimidazole derivatives has been investigated, with a focus on optimizing the performance of conducting doped polymers. Through designing and synthesizing air-stable dopants with different SOMO energy levels, we demonstrated that an increase of the dopant SOMO energy by only ~0.3 eV enhances the electrical conductivity of a benchmark electron-transporting naphthalenediimide–bithiophene polymer by more than 1 order of magnitude.

Additionally, the low thermal stability of the electronic properties of doped polymers still represents a significant obstacle to implementing these materials into practical applications. We report on the sequential doping of poly(benzimidazobenzophenanthroline) (BBL) with a benzimidazole-based dopant, which results in excellent long-term stability at elevated temperatures. We observed that the electrical conductivity of the doped polymer remains unchanged even after 20 hours of heating at 190 °C. This is of particular interest for organic thermoelectrics and provides insights into the low thermal stability of the electronic properties of doped polymers.

Finally, the interfacial energetics are known to play a crucial role in organic electronic devices. However, their effects in organic thermoelectrics remain to be elucidated. We report that the output power density of an OTEG at ambient atmosphere can be greatly improved, by fine-tuning the metal-polymer interface. This emphasizes the importance of understanding the metal-polymer interface in the design of efficient and stable OTEGs.

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Topic: Thermoelectric Materials & Processing (MP)
Oral Presentation *MP.01*

Textile-based wearable TEG by electrochemical coating of felt fibers with conductive polymers

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The Internet of Things (IoT) concept has promoted the development of wearable electronics such as smart fabrics and implantable medical devices. However, most of these devices use batteries as power sources, subject to periodic recharging and replacement. Therefore, the next challenge is to design new systems to obtain sustainable energy to generate power for portable electronic devices [1]. One way is by harvesting it from the human body, which can be considered a constant and uninterrupted energy source for portable power devices. Most human energy is released in the form of heat, so it is reasonable to use thermoelectric generators (TEGs) to harvest thermal energy and convert it into electrical energy. Reimer et al.[2] estimated that the total heat dissipated by the human body ranges from 60–180 W. However, harvesting all this power would require coating the entire body with thermoelectric generators, limiting their practical use. So, it is more reasonable to design TEGs to occupy a small body part, maximizing efficiency. For the efficient design of wearable thermoelectric generators, it must be considered the body position in which the wTEG will be placed since the generation of body heat is related to metabolic activity [3].

Textiles have great potential for obtaining wearable thermoelectric generators (T-wTEGs) as they help to improve the portability of TEGs. In general, the advantage of using textiles to integrate TEGs lies in their comfort, adaptability to movement, and guaranteed heat transfer [4, 5]. In recent years, the researchers promoted the development of T-wTEGs by using alternative materials such as conductive polymers, which are biocompatible, flexible, and lightweight. The elasticity and plasticity of conductive polymers are similar to those of ordinary yarns, which should prevent delamination and fragmentation when bending or twisting coated textiles [5]. In addition, due to the low thermal conductivity of conductive polymers, they are ideal candidates to quickly and economically obtain efficient T-wTEG.

In this work, we have developed a method for coating textiles with conductive polymers by electrodeposition and then we ave elaborated a T-wTEG with the textile obtained. The adhesion of conductive polymers to flexible substrates is generally low, and therefore, we first coated the fibers with carbon nanotubes (CNTs) using the Layer-by-Layer (LbL) technique. Compatibilizing agents used to disperse carbon nanotubes help make CNTs firmly adhere to textile fibers. Once the fabric is coated with carbon nanotubes, it is possible to use it as a working electrode and carry out electrodeposition of conductive polymers. The felt fabric was coated with MWCNT and PEDOT with different counterions (ClO_4, PF_6, and BTFMSI). Since the coating of PEDOT:BTFMSI has the best thermoelectric performance, we chose this coating to manufacture a wearable thermoelectric generator (wTEG) with a bracelet shape. The prototype consisted of 14 thermoelectric units connected in series, in which the final open-circuit voltage and resistance are equal to the sum of the voltage and resistance of each unit, respectively. The basic thermoelectric unit was made with ten pieces of felt coated with MWCNT and PEDOT:BTFMSI (10 x 5 mm) connected in parallel to reduce the final resistance (Fig. 1(a)). The initial resistance of each piece was around 8 Ω, and the final resistance of one basic unit was 1.2 Ω. After connecting the 14 units, the designed thermoelectric generator gave

a total resistance of 16.5 Ω. The textile-based wearable thermoelectric generator (T-wTEG) was thermally contacted with thermal paste, and different thermal gradients were applied to evaluate the power output Fig. 1(b). The power output obtained by the wearable thermoelectric generator developed in this work, 6.5 μW at ΔT =57 K, Fig. 1(c) and (d), is superior to many of the textile-based TEGs reported. Therefore, the method presented in this work based on the electrochemical coating of textile fibers/MWCNTs with PEDOT:BTFMSI has enormous potential for further development on T-wTEGs due to fact that the resulting internal resistance is very low maximizing the final power output.

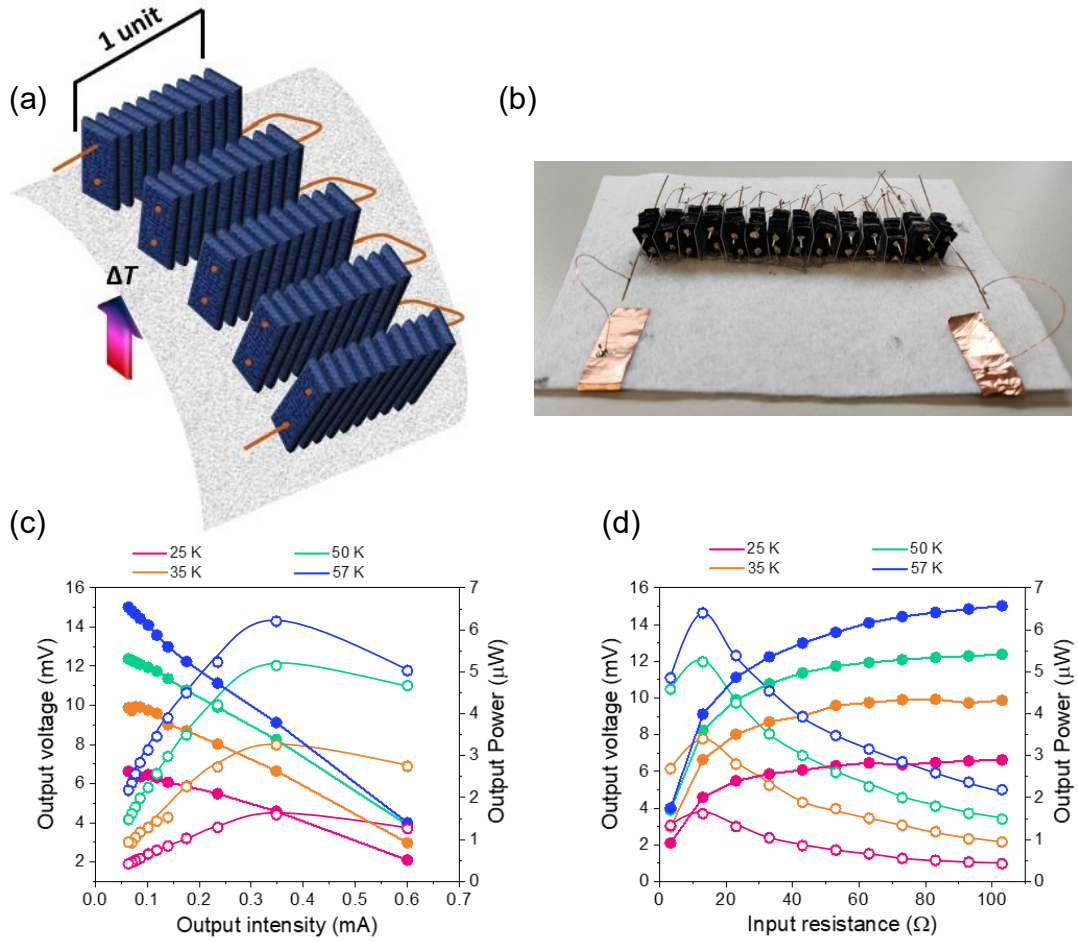

Fig. 1. (a) Scheme of the TEG. (b) Real TEG photograph. TEG characterization as a function of (c) output intensity and (d) input resistance. Open dots for Output Power and full dots for Output voltage.

The authors acknowledged the financial support of the Advanced Materials Program (grant no. MFA/2022/064), supported by the Spanish Ministry of Science and Innovation with funding from the European Union (NextGenerationEU, PRTR-C17.I1) and by the Generalitat Valenciana.

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Topic: Thermoelectric Materials & Processing (MP)
Oral Presentation *MP.02*

Thermoelectric properties of layered nanocomposites based on conducting polymers

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Thermoelectricity has become a very interesting topic in the framework of energy harvesting. Historically, inorganic materials have dominated the thermoelectric applications. However, organic and hybrid semiconductors such as: conducting polymers and nanocomposites based on carbon materials (CNTs or graphene) are now considered promising candidates for the next generation of thermoelectric materials. Their thermoelectric efficiency, measured by the dimensionless figure of merit ZT ($ZT=S^2\sigma T/\kappa$ where S, σ and κ are the Seebeck coefficient, the electrical and thermal conductivities, respectively) has been improved several orders of magnitude, with values currently very close to the inorganic materials. In addition, conducting polymers and nanocomposites based on carbon materials present several advantages over inorganic materials such as: renewable raw materials, lack of toxicity, low cost of production and etc. Single wall carbon nanotubes (SWCNTs) and double wall carbon nanotubes (DWCNTs) are widely used for producing thermoelectric nanocomposites due to their good electric properties. However, processing this type of nanostructures into homogenous films is challenging due to problems related to the stability in water based suspensions and dispensability in polymer matrices. Therefore, Layer-by-layer (LbL) assembly has been gaining attention as one of the most promising techniques to develop nanostructured materials being possible to combine different materials such as conducting polymer nanoparticles and carbon nanostructures by electrostatic interactions in thin films. This method showed excellent results in terms of thermoelectric efficiency being possible to increase the electrical conductivity and the Seebeck coefficient simultaneously [1].

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Topic: Thermoelectric Materials & Processing (MP)
Oral Presentation *MP.03*

Unexpected abrupt bond lengthening in GeTe as the origin of the anomaly in the experimental Seebeck coefficient

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Thermoelectric materials enable the direct and reversible conversion of a heat gradient into electrical power based on the Seebeck effect, thus holding the promise to help create a greener and eco-friendlier energy economy. The performance of these materials is assessed by the thermoelectric figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the total thermal conductivity, which is composed by the electronic and lattice contributions.
Tellurium-based compounds have always been historically among the best thermoelectric materials, with figures of merit exceeding the value of ~2 [1]. We have established arc-melting as a direct procedure to synthesize straightforward, fast, and inexpensively, different tellurides like, for instance, GeTe. The germanium telluride is a chalcogenide material which presents interesting features for thermoelectricity, such as a relatively complex band structure and a phase transition from a rhombohedral to a cubic structure at a temperature near ~700 K. A phase transition in a thermoelectric material is a double-edge sword, since it is undesired for practical device operation, but the fluctuations near this phase transition can be favorable for thermoelectric performance.
Using NPD and SXRD, we have analyzed the structural evolution from room temperature up to 783 K, finding unexpected anomalies involving the abrupt Ge-Te bond lengthening accompanied by increased Te thermal displacements. We have also been able to correlate this phenomenon to the anomaly observed in the experimental Seebeck coefficient [2].

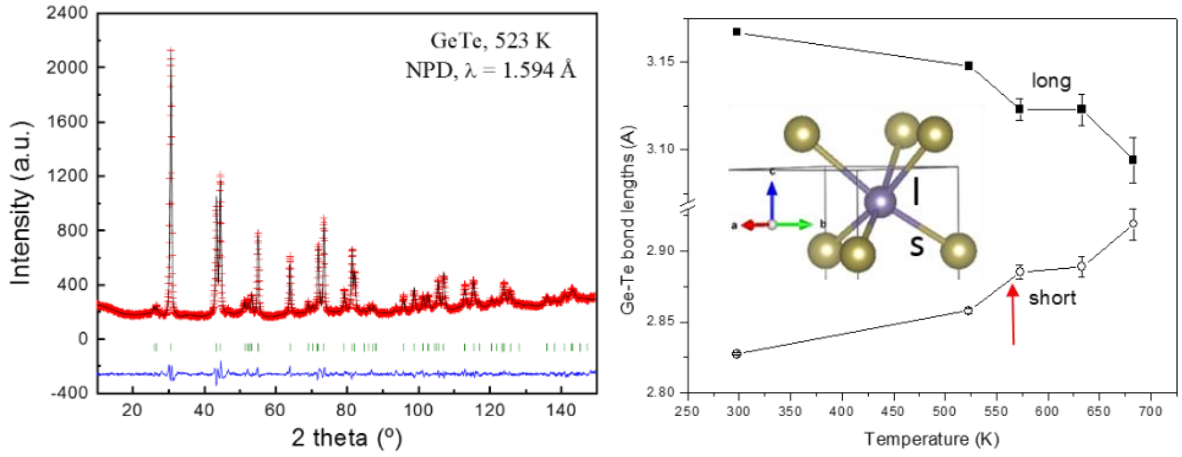

Fig. 1. Left: NPD pattern of rhombohedral GeTe. Right: Short and long distances of the GeTe6 octahedra.

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Topic: Thermoelectric Materials & Processing (MP)
Oral Presentation *MP.04*

Investigation of the low-temperature thermoelectric transport and intrinsic electronic structure of half-Heusler TiCoSb

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In an energy-sustainable context, thermoelectric materials offer the remarkable capability to convert heat gradients into electrical energy and *viceversa*. In the last decade, the investigations on the intrinsic electronic structure of thermoelectric materials[1] have brought forward encouraging enhancements of the energy conversion performance. More precisely, band structure engineering has a strong beneficial impact on thermopower and conductivity optimization, and to implement it, the electronic structures are theoretically determined and analysed. Among promising thermoelectric materials, half-Heusler alloys exhibit a high performance at high temperatures and a variety of compositions with complex band structures[2]. Several reports reveal that disorder and defects in the TiCoSb $C1_b$ type structure are still under discussion[3–5]. Those are recognized as the main factors determining the electrical transport in this material, altering the band structure as forming in-gap states, modifying the Fermi level (E_F), and acting as scattering centers. Thus, TiCoSb properties has shown significant deviations depending on its preparation conditions[3–5].

Here, we have grown TiCoSb half-Heusler single crystals to allow the experimental angle-resolved photoemission spectroscopy (ARPES) analysis of the electronic structure. The thermoelectric transport properties have been measured as well, showing a stark sensitivity to crystallographic defects within samples, while hard X-Ray spectroscopy (HAXPES) allows us to discard interstitial defects which could induce in-gap states. Single crystals of TiCoSb show p-type transport, in contrast to the n-type behaviour found in polycrystalline studies. Still, slight differences in the defect concentration of two different crystal batches, which were prepared by an identical method, display distinct metallic and semiconductive behaviours, even though the elemental analysis could not find any compositional difference. Thus, each of the crystal batches present a different effective mass, which is in agreement with the electronic structure and band convergence picture found by ARPES. This investigation provides new insights on the strong impact of point defects on the optimization of thermoelectric properties.

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Topic: Thermoelectric Materials & Processing / Theory and Modelling (MT)
Invited Oral Presentation *I.04*

High-pressure synthesis of thermoelectric materials

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In this talk, I will describe different families of thermoelectric materials that can be stabilized at moderate pressures 2–3.5 GPa in a piston-cylinder press. The synthesis of some of these systems had been previously reported under higher hydrostatic pressures (6–10 GPa), but can be accessed under milder conditions in combination with reactive precursors prepared by soft-chemistry techniques. These systems include perovskite oxides with transition metals in unusual oxidation states, such as RNiO$_3$ with Ni^{3+} (R = rare earths); pnictide skutterudites M_xCo$_4$Sb$_{12}$ (M = La, Yb, Ce, Sr, K) with inhomogeneous filling factor at the structural voids (2a sites); oxychalcogenides with chalcopyrite structure (e.g. BiCuOSe) or black phosphorous, to quote some. The availability of substantial amounts of sample (0.5–1.5 g), already sintered in pellets, allows a complete characterization of the thermoelectric properties (viz., Seebeck coefficient, thermal and electrical conductivity), as well as the structural analysis by neutron, synchrotron X-ray diffraction, and X-ray absorption spectroscopy techniques.

As a brief overview, the high hydrostatic pressure favors the formation of the short and strongly covalent chemical bonds characterizing the high oxidation states; on the other hand, the pressure prevents the decomposition of unstable reactants at the synthesis temperature and the oxidation or volatilization of certain reactants (typically P, As, Sb, S, Se, Te…). Those factors act to increase the coordination numbers and to enable the achievement of denser phases in perovskite-like materials, skutterudites, etc. Finally, the high pressure enhances the reaction kinetics substantially. All those features make the high-pressure synthesis methods a good and promising choice to prepare novel compounds with a low stability or a metastable character.

Microwave-assisted synthesis of thermoelectric chalcogenides

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The remarkable increase in global energy consumption and the current climate crisis has promoted research into new and efficient approaches for energy generation. In this context, thermoelectric technology has an important role because of their ability to convert waste heat into electrical energy. Nevertheless, the low conversion efficiency of commercial thermoelectric devices, as well as the high toxicity and scarcity of the constituent materials (Bi_2Te_3, Sb_2Te_3, PbTe…) hinder their large-scale implementation [1]. This motivates research into materials that are more environmentally friendly, abundant and highly efficient. On the other hand, sustainable synthetic routes based on "soft chemistry" or "fast chemistry", which follow the principles of "green chemistry", are currently strongly appealing for the preparation of thermoelectric materials rather than the traditional ceramic method.

Among the alternative synthesis methods, microwave-assisted hydrothermal synthesis has emerged as a powerful route to prepare thermoelectric chalcogenides. The use of microwaves makes possible an efficient, uniform and direct heat transference owing to remarkable coupling of the microwave to the polar molecules in the solution (*e.g.*, water), and therefore allows the increase of the crystallization kinetic [2]. Furthermore, processing time by this route (minutes) is noticeably shorter than the ceramic technique (days), which results in energy savings.

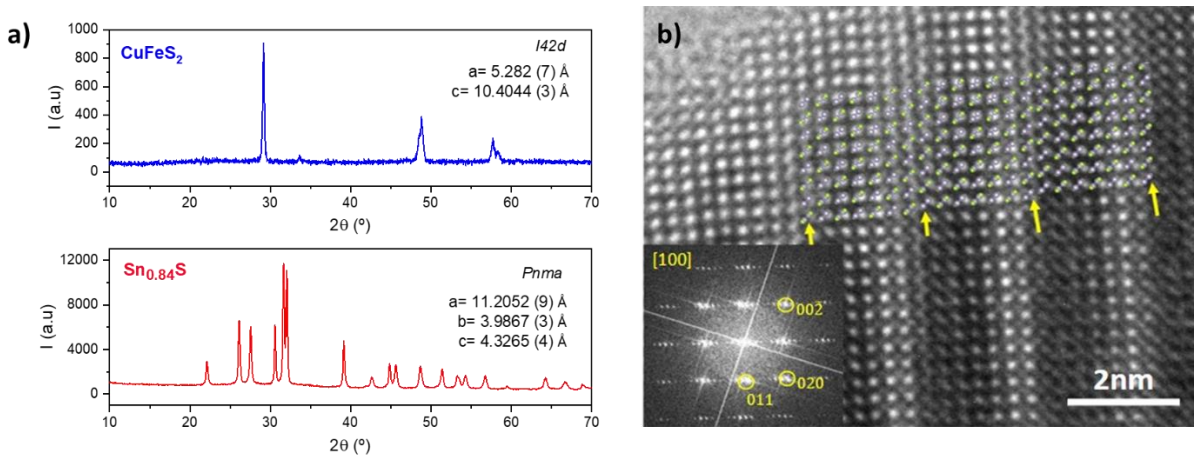

Fig. 1. a) X-ray diffraction patterns of $CuFeS_2$ (blue) and $Sn_{0.84}S$ (red) prepared by microwave-hydrothermal synthesis; b) HRTEM image of $SnS_{0.8}Se_{0.2}$ crystal along the [100] zone axis. The FFT in the inset shows extra spots observed along 0–11 confirming the modulation of the structure.

Herein, an ultra-fast microwave-hydrothermal synthesis of pure polycrystalline phases of $SnS_{1-x}Se_x$ (x=0, 0.1, 0.2, 1) and $CuFeS_2$ is shown. In the case of SnQ (Q = S, Se) samples, one minute of microwave irradiation is enough to synthesize the compounds. This allowed the generation of randomly distributed tin vacancies in the crystal structure (Sn:Q ≈ 0.84:1), as demonstrated by synchrotron X-ray diffraction. This phenomenon influences the physical properties of the

synthesized compounds by modifying the concentration and mobility of the charge carriers [3-4]. Furthermore, chalcopyrite $CuFeS_2$ sample, which is considered a promising thermoelectric material when its lattice thermal conductivity κ_{lat} is successfully reduced, can also be efficiently produced in minutes.

In this communication, synthetic aspects, structural and microstructural characterization as well as the thermoelectric properties of the aforementioned phases will be presented.

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Topic: Thermoelectric Materials & Processing / Theory and Modelling (MT)
Oral Presentation *MT.06*

Co-doping tetrahedrite: impact of Nickel and Selenium in thermoelectric properties

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For several decades, despite extensive research, the wide application of thermoelectric generators had seemingly been a piped dream, as other heat conversion technologies were more efficient and cheaper, with the added benefit of not relying in highly toxic and increasingly rarer thermoelectric materials, like those based in Bi, Pb and Te. Thus, the application of thermoelectric devices was reduced to very specific niche fields, where durability, reliability or compactability were prioritized.
Recent advancements in material sciences and computational models capable of better simulating transport properties in solids, changed this perspective. Thermoelectric materials are now being more intensively researched, as new materials are being discovered with each passing year. For the most part, these materials cannot yet replace conventional materials, as their thermoelectric performance is still lower. However, most of the new materials are far more cheap and less toxic than the classic (Bi, Pb and Te-based) ones.[1]
Tetrahedrite ($Cu_{12}Sb_4S_{13}$), an earth-abundant mineral, is one of these novel, cheaper and more sustainable thermoelectric materials, which has been growing in popularity. An ample research has been carried out to improve the already naturally good pristine properties, because of its abnormally low thermal conductivity, by fine tuning the composition by introducing dopants or adjusting the content of each element. [2]
Generally, the studies conducted on tetrahedrite focused on a single dopant or varying a single element, while those conducted by simultaneously doping with two different elements are sparse. Thus, in the present study, the impact of Ni and Se in both the thermoelectric properties and in phase composition will be presented, both experimentally and simulated with Wien2K and BoltzTrap softwares. [3,4]
The characterization of the samples with various contents of Ni and Se, following the formula $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$, revealed samples after casting and after annealing to be mainly composed of tetrahedrite phase with some occasional secondary phases of copper/nickel sulphides and chalcostibite ($CuSbS_2$). SEM-EDS, powder X-ray and Raman spectroscopy revealed that both Ni and Se were integrating the tetrahedrite matrix, with the semi-quantitative EDS analyses placing the actual composition of these samples to values very similar to what was expected.
Both simulations and experimental measurements pointed to an optimum composition around $Cu_{11.5}Ni_{0.5}Sb_4S_{12.5}Se_{0.5}$. According to the simulations, it would have a figure of merit around 0.30 at 300K, and an experimental power factor of 1280 $\mu W/m.K^2$ was obtained, which, after estimating thermal conductivity with the Wiedemann-Franz law, resulted in a figure of merit of ~0.32 at 300K.

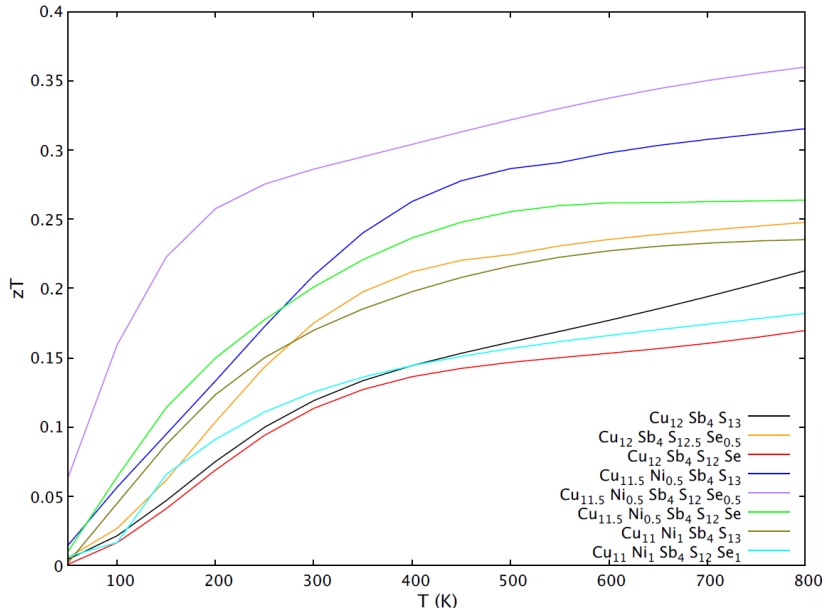

Fig. 1. BoltzTrap simulations of the figure of merit for various tetrahedrites with different Ni and Se content, based on the chemical formula $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$.

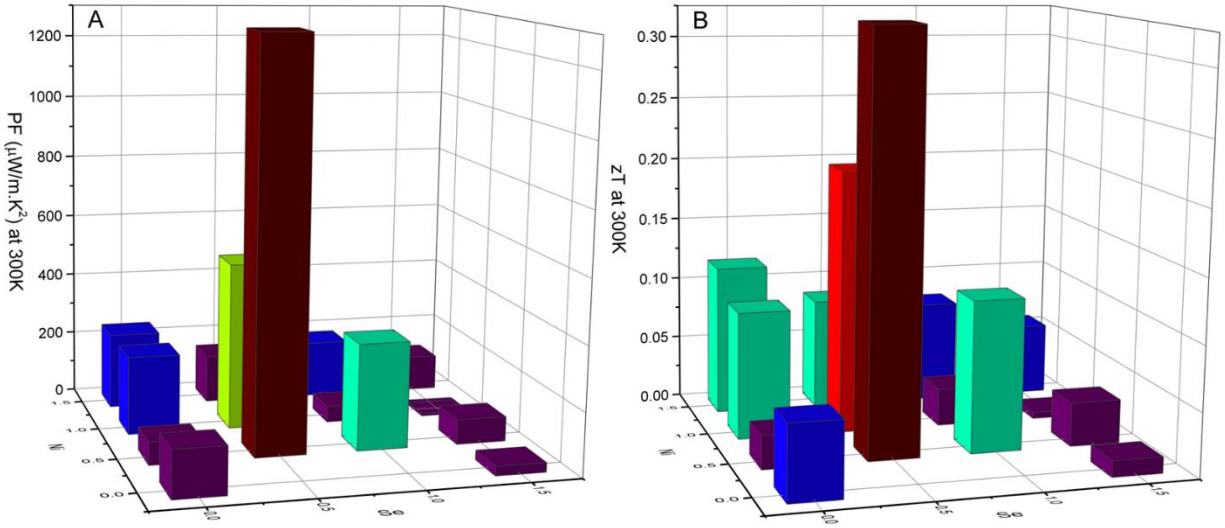

Fig. 1. Calcuted Power factor (A) and figure of merit (B) with the experimental measurements of the Seebeck coefficient and electrical resistivity of the annealed samples with the formula $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$.

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Physical Insights on the Chemical Factors that Influence the Thermoelectric Properties in Cu- and Ag- based Sulvanites

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Traditionally, the search for more efficient and affordable thermoelectric (TE) materials relied on discoveries through repetitive experiments involving synthesis, characterization, and property measurement. Computational methods were only used retrospectively to gain insight. However, recent developments in computational techniques, such as high-throughput frameworks and machine learning algorithms combined with density functional theory (DFT) methods, have allowed for the optimization of TE efficiency and a better understanding of the physicochemical factors governing thermoelectricity. In this study, we apply a rational design approach to sulvanites, which are a group of ternary copper chalcogenides Cu_3MX_4 (M = V, Nb, Ta; X = S, Se, Te) consisting of Earth-abundant, non-toxic, and sustainable elements. Sulvanites have shown promise for use in thin film photovoltaics [1] and TE technologies [2], and their facile synthesis via standard solid-state [3] methods make them even more desirable. However, despite their potential, experimental data on the TE properties of Cu-based sulvanites are scarce and, as well as the few theoretical studies available, limited to a few members of the family in most studies and, in no case, there is a rationalization of the trends found in κ_l (se Fig. 1) in terms of the chemical composition of these materials. Our focus here is on understanding the factors affecting phonon thermal transport, which is crucial for the rational design of new materials with excellent TE properties.

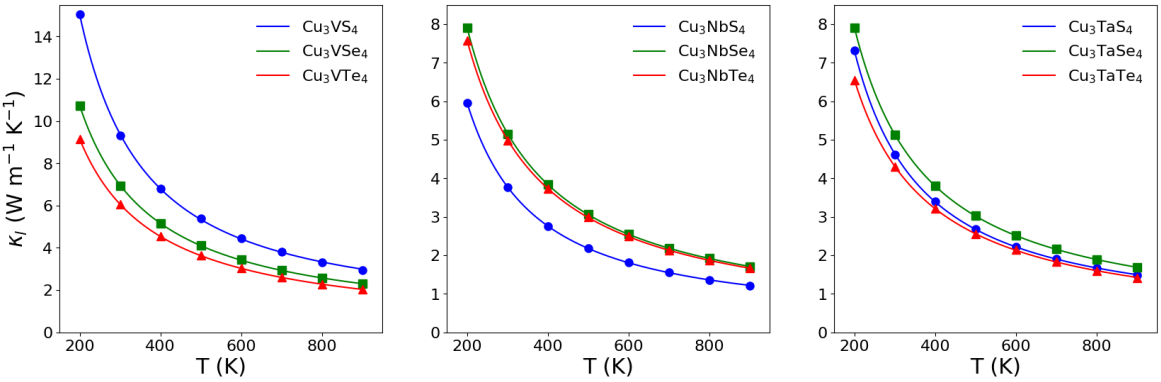

Fig. 1. Calculated lattice thermal conductivities of copper-based sulvanites.

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Topic: Thermoelectric Materials & Processing / Theory and Modelling (MT)
Oral Presentation *MT.08*

$SrTiO_3$ – based thermoelectrics prepared by Laser Floating Zone technique

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Global energy consumption is expected to continue increasing, and the need for more efficient and renewable sources for energy production is essencial to assure energy demands are achieved without environment degradation and/ or over relying on finite resources [1]. Thus, green energy production and energy-efficient technologies are necessary. Thermoelectric (TE) energy harvesting can become one of the viable solutions to increase the efficiencies of various high-temperature industries [2]. For this, highly-performing TE materials are fundamental. Traditional and commercialized TE mostly are not stable at higher temperatures and harsh environments. Consequently, TE oxides are expected to be a prime candidate for these applications due to their high chemical and thermal stability [3]. Despite these advantages, most oxides usually show lower ZT values when compared with "traditional" thermoelectrics. Still, it can be overcome by designing new compositions and micro-/nanostructures, and involving new processing techniques leading to increases in TE oxide performance [4]. Amongst the studied families of oxides for TE applications, $SrTiO_3$ -based TE are among the most promising, with a composite composition, STN + 0.5% reduced graphene, achieving a ZT value of 1.42 [5]. In this work, we demonstrate a new approach to prepare $SrTiO_3$-based TE materials using the Laser Floating Zone (LFZ) technique. LFZ processing offers a number of advantages for TE materials like high density, uniform distribution of the cations composition in the melt, tunable phase formation and cation distribution controlled by the cooling rate, as well as LFZ processing could be an attractive technique for high-volume production [6]. This study analyzes and characterizes the effects of growth rate and thermal post-treatment on relevant structural and thermoelectric properties of donor substituted $SrTi_{1-x}Nb_xO_3$. The results indicate the ability to prepare these materials by LFZ, resulting in mechanically strong fibres with adequate electrical and TE properties. The post-annealing resulted in a considerable increase in electrical conductivity and relatively high power factor values of the samples, derived from the further reduction and consequent charge carrier generation.

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Topic: Devices & Applications (DA)
Invited Oral Presentation *I.05*

Advancements in Laser Floating Zone processing for optimizing the thermoelectric properties of oxide materials. Properties

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Abstract.

Transition oxides-based ceramics are known as potential alternative thermoelectric materials in scenarios where high thermal and chemical stability are required. Many oxides also allow flexible tuning of the relevant electrical and thermal transport properties through doping/substitution and by using specific processing approaches. This work discusses the prospects for growing oxide-based thermoeelctrics by the laser floating zone (LFZ) technique assisted by an external magnetic field. Various opportunities for tuning the structural, microstructural and thermoelectric properties are explored. This technique allows the growth of fully dense fibres, as well as the formation of metastable phases and/or promoting different oxidation states by adjusting the growth conditions under various pulling rates and using different growth atmospheres. The external magnetic field was found to promote notable variations of the microstructure and phase composition of the LFZ-grown fibers. The obtained guidelines suggest that LFZ is a suitable technique for processing thermoelectric oxides, if optimized control over growth parameters and re-equilibration conditions is imposed.

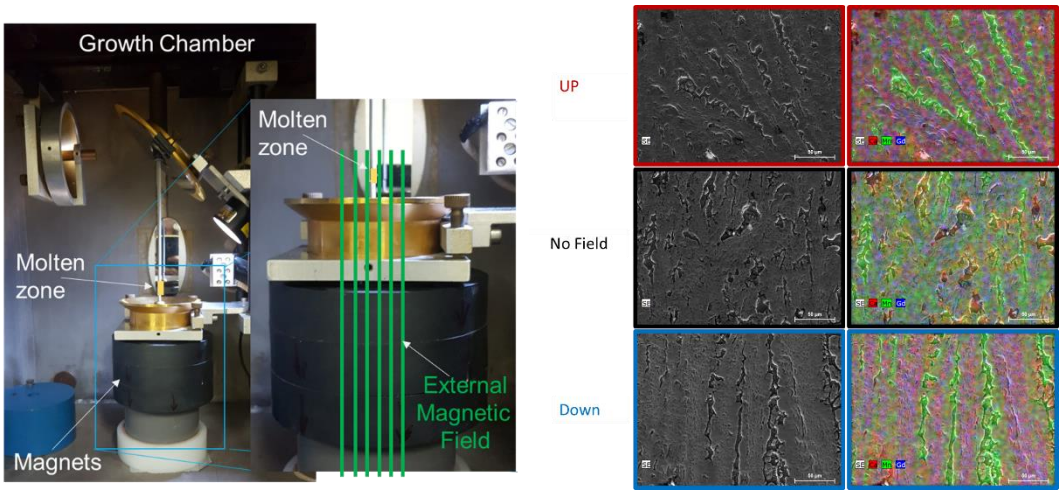

Fig. 1. Magnetically Assisted Laser Floating Zone setup and microstructural effect on field direction.

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Topic: Devices & Applications (DA)
Oral Presentation *DA.06*

The Impact of Collectors/Absorbers on the Efficiency of PhotoThermoelectric Devices

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Collectors and/or plasmonic systems can be used when combined with electromagnetic waves to increase the temperature promoting temperature gradients to be used in thermoelectric generators (TEGs) [1]. The influence of different screen-printed collectors will be investigated in this work to understand how they affect the ultimate performance of the TEGs. Several radial printed TEGs were created for this purpose, employing 8 thermoelectric stripes manufactured using commercial *p*-type chalcogenide Sb_2Te_3-based inks [2]. The radial arrangements allow us to integrate the different absorbers/collectors in the device's core. As a result, with this thermoelectric design, a long-distance near-infrared fiber laser with a wavelength of 1450 nm hits its center, causing heat to flow straight along the thermoelectric printed stripes from the inside to the outside of the TEG. Different laser powers were used to generate temperature gradients in the photo-TEG (P_{laser} from 0.15 W to 1 W). Herein, commercial carbon black, titanium nitrate, zinc oxide, and bismuth oxide (Bi_2O_3)-based inks were employed for the absorbers or collectors-based systems. To better understand the impact of the produce absorbers or collectors on the efficiency of the TEGs, a comprehensive characterization of the production devices was conducted before and after the deployment of each collector. Bering in mind the implementation of this systems in the CubeSat technology, all the TEGs are characterized under extreme conditions namely in vacuum (~10^{-6} Torr). Additionally, all the printed collectors were analyzed by UV-Vis-NIR spectrophotometer reaching an absorbance higher than 60%. We will demonstrate that implementing a collector can boosted the produced temperature gradient by 50%, resulting in a 47% boost in total performance. Ultimately, the technological viability of such hybrid systems, such as high-resolution sensors in high-wavelength lasers (Near-infrared Region), will be discussed.

Acknowledgements: Financial support from UIDB/04968/2020, and NORTE-01-0145FEDER-022096 from NECL is gratefully acknowledged. ALP, MMM, MR and AMP thank the funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 863307 (Ref. H2020-FETOPEN-2018-2019-2020-01). MMM thanks FCT for grant SFRH/BD/144229/2019.

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Topic: Devices & Applications (DA)
Oral Presentation *DA.07*

Wireless Energy Transfer Using Printable Devices based on Thermoelectricity: from Concept to Application.

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Since Maxwell's discovery of magnetic induction over 200 years ago, the subject of off-grid power transfer has persisted. Since then, other projects have been launched to strengthen current processes or cutting-edge technologies. The drawback with magnetic induction that it is highly effective but it imposes a set against the backdrop on the distances over which this transfer of energy could be achieved. The dimensions of the coils that create the magnetic field flow that can transport energy from one side to the other without contact are constrained, which is primarily the cause of this limitation. The employment of electromagnetic light waves using lasers and employing them as the transducer of this electromagnetic wave to transport energy into the body is another innovation that has arisen as a rival to magnetic induction. Due to their use as solar panels, photovoltaic panels have, however, already been developed for the visible zone. However, for long distance transfers (of the order of km), lasers of wavelengths of the order of micrometers must be employed. and indeed the cells are not established for high conversion efficiency in this range of the near infrared spectrum.

As a consequence, our group has been working on the development of a long-range energy transmission system employing thermoelectric-based photoenergy converters as half of the WIPTHERM project using fiber optics lasers with wavelenght of 1.5 um. This study will outline the envisioned system's scientific and technical grounding together with the investigation that have done on the microfabrication of the devices using printing techniques under flexible substrate. The manufacturing of printing pastes comprising organic and inorganic materials, interfaces for thick films (tens of micrometers) will be discussed. Finally, we shall list the ideas and experiments that have been done at longer distances, such as those of about 70 meters. The possibility of application in space, namely in nanosatellite systems, will also be hilighted namely the efficiency under low temperatures (~150K) and under vacuum (10^{-6} mBar).

Acknowledgements: Financial support from UIDB/04968/2020, and NORTE-01-0145-FEDER-022096 from NECL is gratefully acknowledged. ALP, MMM, MR and AMP thank the funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 863307 (Ref. H2020-FETOPEN-2018-2019-2020-01). MMM thanks FCT for grant SFRH/BD/144229/2019.

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Field operation and modelling of thermoelectric generators for high enthalpy geothermal anomalies

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In the current climate and energy context, it is important to develop technologies that permit increase the use of renewable sources such as geothermal energy. Enhancing the use of this renewable source is particularly important in some places, due to its availability and the enormous dependence on fossil fuels, as is the case of the Canary Islands [1,2]. This work proposes the use of thermoelectric generators with heat exchangers working by phase change to transform the heat from the shallow high temperature geothermal anomalies on the island of Lanzarote directly into electricity, since the use of conventional geothermal power plants would not be possible because they would damage the protected environment [3]. To bring this proposal to reality, this work has succeeded in developing and field-installing two geothermal thermoelectric generators (GTEGs) adapted for two different level of temperatures (medium and high) that operate without moving parts thanks to their phase-change heat exchangers. These robust generators do not require maintenance nor auxiliary consumption, and produce a minimal environmental impact, are noiseless, and the use of water as working fluid make them completely harmless.

After characterizing the hot and the cold side heat exchangers working by phase change, the generators were tested in the laboratory. Tests were carried out with different temperatures in the wall of the TPCT, and varying the number of thermoelectric modules installed in the high temperature generator. Foreseeing that the GTEG for high temperature (HT) would generate more electricity, it was built with 8 TEMs, while the one for medium temperature (MT) was built with 16 TEMs. After checking their satisfactory performance in laboratory, the developed GTEGs were successfully installed in Timanfaya National Park, Lanzarote (Spain), with gases reaching 170 in MT and 465 °C in HT [4, 5].

Both generators have been working for more than 24 months in perfect conditions. The installed hot and cold side heat exchangers are very efficient, with low thermal resistances, demonstrating that phase change heat exchangers are completely adequate for this application, as they transport heat very efficiently and they do not require moving parts nor auxiliary consumption. Thanks to that, each GTEG is generating per year more than 280 kWh. However, the power per thermoelectric module in high temperature doubles the one in medium temperature.

Once demonstrated the viability of this technology, a computational model was developed with the aim to permit the design of a higher-scale installation. The model was successfully validated thanks to the experimental results, with relative errors of ±10% in terms of power and reaching errors lower than 1.6% in medium temperature and 0.5% in high temperature when predicting the annual energy generation.

This research demonstrates not only the viability of this technology to generate clean energy in an area with geothermal anomalies, with very favourable results in terms of energy generation, but also the great potential that exists for transforming the geothermal energy of the island of

Lanzarote into renewable electricity. Furthermore, these robust generators do not require maintenance nor auxiliary consumption, which reduces their costs, producing a minimal environmental impact, noiselessly, and the use of water as working fluid makes them completely harmless.

Acknowledgments

We would like to acknowledge the support of the Spanish State Research Agency and FEDER-UE under the grants TED2021-129359B-I00 and PID2021-124014OB-I00.

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Topic: Devices & Applications (DA)
Oral Presentation *DA.09*

Flexible carbon-based thermoelectric generator with a phase change material for cold-chain monitoring

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A realistic transition to renewable energy sources, such as solar, wind energy, etc., also requires a greater integration of differentiated energy harvesting and saving technologies [1]. In this context, thermoelectric power can play an important role, and be harnessed in several applications of practical interest [2]. Here, we propose an application for cold-chain monitoring of high value-added products that require to be preserved at controlled temperatures throughout the distribution chain. This is in fact a fundamental and ever-growing necessity in the industry of production and distribution of many essential goods, such as food and pharmacy products.
Specifically, we propose a sensor based on a thermoelectric generator (TEG) embedded in a flexible substrate the size of a credit card that can be applied directly to the product to be monitored (Fig. 1a). The working principle is based on the presence of a phase change material (PCM) on one side of the TEG, while the other is directly exposed to the surrounding environment (Fig. 1b). In this way, as long as the product is kept at a correct temperature, both sides of the generator are at the same temperature, and there is no thermoelectric power generation. On the other hand, if the product is exposed to an out of range temperature, one side of the TEG will rapidly evolve towards that temperature, while the other side will maintain the temperature of the phase change transition until the PCM has melted completely. This allows the creation of a transient temperature difference, resulting in the generation of an electrical voltage that can be detected by an external circuitry. The time evolution of this thermal transient provides information on the amount of energy exchanged with the environment, thus providing additional information than merely the exceeding of the maximum allowed temperature. To have practical utility, the whole sensor must be inexpensive and employ sustainable materials. For these reasons, we used paper as substrate because of its low cost, flexibility and recyclability [3]. For the fabrication of the thermoelements we have employed carbon-based materials because they are earth-abundant, compatible with deposition through low-cost, large-area printing and coating techniques, and have suitable mechanical and thermoelectric properties [4].
For the first prototypes, we printed all materials by blade coating using a K Printing Proofer. The p-type elements are deposited starting from a commercial carbon/graphite paste with the addition of wt1% single-walled carbon nanotubes to enhance its thermoelectric properties. For the n-type elements, we further added an n-type dopant (polyethylenimine, wt10%) to the previously described ink. The thermoelectric properties of the materials are obtained on samples with a single thermocouple. Figs. 1c, d show the square resistance and Seebeck coefficient of 5 different TEGs, measured over more than 100 days. As it can be observed (inset of Fig. 1c, d), the average square resistance and Seebeck coefficient are in the order of 7 Ω/□ and 60 µV/K. Moreover, the thermoelectric properties are found to be stable over the observed period, which is a crucial aspect for practical applications. As a first demonstrator, we fabricated a TEG on paper consisting of 12 thermoelements (inset of Fig. 2a), which has an internal resistance of around 700 Ω. Fig. 2a shows the open circuit voltage as a function of the temperature difference applied at the ends of the TEG. Finally, we carried out preliminary measurements on a single p-type thermoelement to evaluate the effect of the PCM. We employed a PCM material with a phase change temperature of 42 ºC. The open-circuit voltage (Fig. 2b) was initially measured by keeping the sample at room temperature, and then

introducing it into an oven preheated to 65 ºC under three different conditions: on the bare sample (gold curve), on the sample with a block of poly(methyl methacrylate) (PMMA3, mm thick) placed on one side (orange curve), and on the sample with a block of PMMA filled with the PCM placed on one side (black curve). While in the first case the voltage is negligible, in the other two cases there is a voltage peak due to the PMMA acting as a thermal insulator, unbalancing the thermal transient between the two sides of the thermoelement. However, the response in the presence of the PCM is different, showing a second peak attributed to the melting of the PCM material. The presence of the PCM generates a larger thermal transient that can be correlated to a sample exposure to an undesired temperature for a certain time. This represents an interesting proof of concept, although a detailed analysis becomes necessary to evaluate the dependence between amount of energy exchanged with the environment and the volume of the PCM, before extending this approach to an entire TEG for the application of interest.

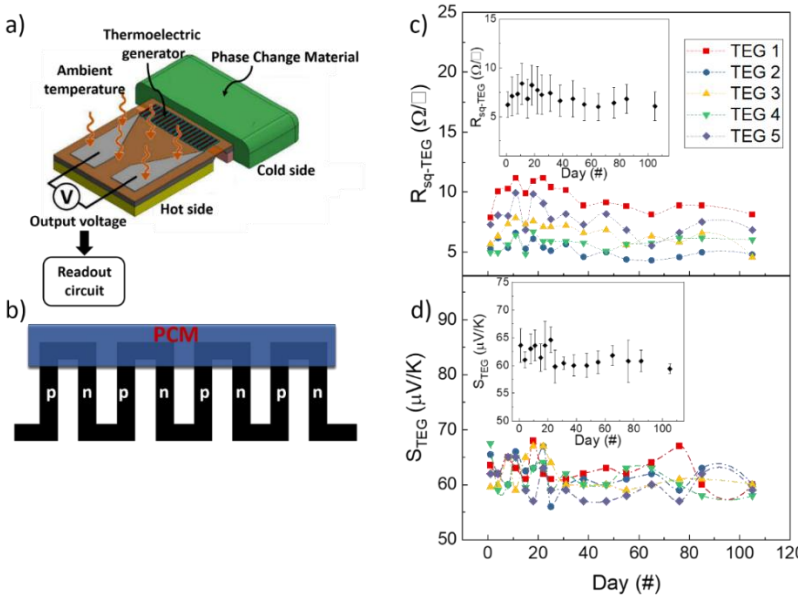

Fig. 1. Schematic representation of the device (a) and detail representing the structure of the TEG (b). Square resistance (c) and Seebeck coefficient (d) of 5 different thermocouples over more than 100 days. The insets show the respective mean values over time (the error bars are the standard deviation).

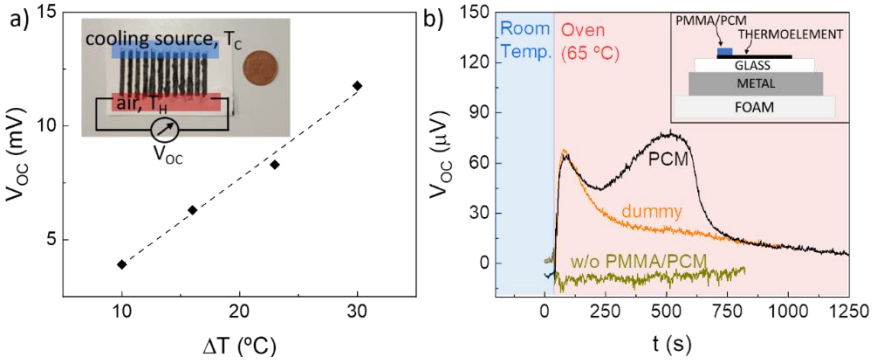

Fig. 2. (a) open circuit voltage of a TEG on paper as a function of the temperature difference. In the inset, a photograph of the TEG. (b) Evolution of the open circuit voltage of a single thermoelement initially measured at room temperature and then placed at 65 ºC under different measurement conditions: exposed (gold curve), covered with a dummy PMMA square (orange curve), and covered with a PMMA block filled with the PCM (black curve). In the inset, a schematic cross section of the device under measurement.

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Topic: Devices & Applications (DA)
Oral Presentation *DA.10*

Prospects of volcano surveillance powered by thermoelectric generators: the Antarctica challenge

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Thermoelectric generators have recently arisen as a solution to guarantee a robust, compact and reliable power supply for volcanic vigilance stations, which are indispensable to predict eruptions. These stations are normally located in areas with access difficulties, lack of power grid, and adverse meteorological conditions. Nonetheless, in those areas it is always possible to find fumaroles, hot gases that emerge from the ground, since it is one of the characteristics of active volcanoes. Transforming this heat into electricity by means of thermoelectric generators suppose a continuous, robust, compact, scalable, and reliable autonomous power supply. These advantages have been demonstrated with the prototype depicted in Figure 1 that has been in operation since December 2019 in an 83.5°C fumarole at Teide volcano (Canary Islands, Spain) [1]. The prototype is made of high-efficiency heat exchangers based on phase change that maximize power generation with no moving parts. With only two Bi-Te thermoelectric modules, the prototype generates enough energy to measure different variables and emit them to a center located 14 km away, leading to a completely autonomous monitoring station.

Fig. 1. Thermoelectric generator installed at Teide volcano in December 2019.

Although the viability of the proposed solution has been demonstrated for more than three years without maintenance, the present work goes a step further, designing a thermoelectric generator for Deception Island (Antarctica). The conditions in this island are extremely harsh, and yet to date none of the solutions tested have lasted a complete austral winter. Thus, if the proposed solution overcomes the challenge, new possibilities for thermoelectric generators will arise, becoming a great solution in order to obtain an autonomous power supply in any volcano in the world.

Acknowledgements
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Topic: Thermoelectric Devices & Applications (DA)
Poster Presentation *P.01*

Implementation of Arrays of Thermoelectric Generators for Nanosatellites: Evaluation under Atmospheric and Space Conditions

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The CubeSats Era is revolutionizing space exploration field in the last years. Several areas, such as weather information, space weather, transportation, navigation and security, are evaluating to resort to this technology. The CubeSat market generated $143.7 million in 2017 and is estimated to grow at a CAGR of 13.43% during 2018-2023 [1]. The powering of the CubeSat systems relies on larger solar arrays that still present some limitations such as low efficiency on non-illuminated areas as well as weight problems. Thus, our team purposed an innovative wireless power device using Thermoelectric (TE) Generators arrays combined with a laser and a specific absorber allowing a Wireless Energy Transfer (WET) [2]. Since CubeSats are exposed to continuous temperature changes, e.g., due to changing sun irradiation during orbits, and for materials to be suitable for space applications, their performance under thermal cycling in vacuum must be validated.
Herein, the fabrication of photo-thermoelectric plasmonic (HPTP) system composed of an array of 9 radial thermoelectric generators connected in series was performed by a simple screen-printing process. The TE strips were fabricated using an optimized Bi_2Te_3/polyvinyl alcohol (PVA) ink, while the electrical contacts between them were made using a commercial silver ink. In parallel, the design and implementation of a vacuum cryogenic chamber for performance evaluation of the HPTP as well as validation of the robustness of all components under space conditions is also presented. The cryogenic chamber presents a rectangular-shape being its walls made of an aluminum alloy. This chamber will allow to evaluate the performance of the HPTP measuring the generated voltage over the time while the inside temperature is increase/decrease from 100 to 400 K (vice-versa) under ultra-high vacuum conditions. At room temperature and atmospheric pressure conditions, the HPTP showed a generated voltage output of 40 mV power laser of 4.5 W.

Acknowledgements

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Topic: Thermoelectric Materials & Processing (MP)
Poster Presentation *P.02*

On the Thermal Conductivity of Thermoelectric Polymers Upon Doping

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Understanding the general correlation between electrical and thermal transport in organics is a key element to fabricating high-performance thermoelectric generators.[1] In order to investigate this issue in a systematic fashion, we have looked at eight conjugated polymer materials (PBTTT, DPP-DTT, PDPP4T, NIP3H, NIP3H-BDT, Regio Random P3HT, Regio Regular P3HT, p(g4 2T-T)) and four doping systems, namely, F4TCNQ, FeCl3, FeCl3-Li-TFSI, FeCl3-BMP-TFSI. The thermal conductivity of selected samples was analysed by Frequency-domain thermoreflectance (FDTR)[2]. Upon doping, the out-of-plane thermal conductivity of all five semicrystalline polymers reduces with respect to the neat polymers, while that of the amorphous material increases. As the electronic contribution to the thermal conductivity increases with doping following Wiedemann Franz law[3], the observed reduction in the overall thermal conductivity is intriguing and could be a very interesting feature for thermoelectrics.

Several hypotheses are being investigated, namely an alloying effect of the dopant, a reduction in crystallinity, and an increase in anisotropy (orientation induced by doping). GIWAXS data suggest that the degree of order is not reduced. We managed to produce free standing films of the two DPP-based polymers in order to measure their in-plane thermal conductivity. We found that in both cases, the in-plane thermal conductivity increases upon doping. Our current understanding is that doping induces an increase in orientation within the plane of the film, thus thermal transport within the polymer chain is favoured in the plane, while the two directions of low thermal conductivity, i.e. pi-pi stacking and sidechains, are preferentially distributed perpendicular to the plane of the film, thus reducing the thermal conductivity out-of-plane.

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Topic: Measurement and Characterization
Poster Presentation *P.03*

Impedance spectroscopy: a suitable tool to fully characterize a thermoelectric device

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The fabrication of thermoelectric devices is not a simple task, since it involves the optimisation of many parameters, such as the thermoelectric materials themselves, their connection with the metallic strips, the thermal influence of the electrically insulating layers, etc. Impedance spectroscopy offers many advantages to characterize thermoelectric devices, since from simple measurements that just require the connection of the device to the impedance equipment and vacuum, it is able to quantify many of the key properties of the device, such as the materials properties and the thermal contact resistances at the thermoelectric material/metallic strip junctions [1].

In addition, when integrating the devices into generators the efficiency of conversion of heat into electricity is not only influenced by the material properties, but it also depends on the temperature of operation, which is governed by the thermal resistances from the thermoelectric legs up to the heat source/sink [2]. The thermal contact resistances between the outer ceramics of the thermoelectric devices and the heat exchangers is especially essential. We recently proved that these thermal contacts can be determined by performing an impedance measurement in suspended conditions and a measurement with the device assembled [3]. In this work, we show all the advantages and benefits of the impedance method, and its enormous potential to fully provide all the key properties of a thermoelectric device.

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Topic: Other Topics on Thermoelectricity
Poster Presentation *P.04*

PDADMA-based solid electrolytes to significantly enhance the power factor of a thermoelectric oxide film

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The performance of thermoelectric materials is estimated by the device figure of merit ($ZT=S^2\sigma T/\lambda$, being S the Seebeck coefficient, σ the electrical conductivity, λ the thermal conductivity, and T the absolute temperature). Recently, large power factor ($PF=S^2\sigma$) enhancements have been shown in a novel hybrid solid-liquid thermoelectric system, consisting of a porous nanostructured solid material (Sb-doped SnO_2) in contact with diverse liquid electrolytes [1].

In this contribution, we have investigated the nanostructured Sb-SnO_2 film in contact with different solid electrolytes based on the poly-diallyl dimethylammonium cation (PDADMA). From all the electrolytes tested, the poly-diallyl dimethylammonium chloride (PDADMAC) was found to provide more than 2 times improvement in the power factor. This large improvement was due to a ≈60% decrease in the electrical resistance of the device accompanied by a slight reduction of less than 10% in the absolute value of the Seebeck coefficient. Impedance spectroscopy analysis was carried out to understand the role of the solid electrolyte in the device performance. This notable power factor improvement paves the way to use polyelectrolytes to fabricate all-solid-state hybrid solid-electrolyte devices with enhanced power factors.

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Topic: Thermoelectric Materials & Processing (MP)
Poster Presentation *P.05*

Characterization of a Possible Thermoelectric Material prepared from Natural Pyrite

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Thermoelectric (TE) materials have been the subject of numerous studies for some decades as they can effectively contribute to reducing greenhouse gas emissions, which lowers the environmental impact due to the use of green technologies. Another important aspect is the raw material used in the generation of these materials, and its abundance and availability is crucial [1]. Pyrite (FeS_2) is one of the most abundant minerals in the earth's crust, as well as being easy to extract and inexpensive, which makes it a material of choice for technological developments. By heat treatment of the mineral, it is possible to generate a thin film of magnetite (Fe_3O_4) that confers magnetic properties of the pyrite. Starting from magnetic materials, and using the properties associated with the presence of spins, materials with TE characteristics can be designed [2]. However, for these materials to be efficient, it is necessary to clearly understand the interrelationships between their structure, magnetic behaviour and Seebeck effect. In this work, we prepare and characterise a material with TE properties from a natural mineral. Pyrite single-crystals were sectioned and chemically treated for cleaning. These films were placed at different temperatures and exposure times, under normal conditions of pressure and aerobic atmosphere. The chemical species of each surface film were determined by XPS; the structure and composition of the different materials generated using TEM, STEM, EELS; the magnetic properties by MFM and magnetometry measures and the charge carriers through Seebeck effect. For the 3 exposure temperatures, films with different characteristics were obtained, as well as for the different exposure times. XPS and EELS spectra, revealed the presence of oxidised Fe and Oxygen species. TEM and STEM images revealed different structural arrangements for the magnetite: amorphous thin film, epitaxial formation and nanoparticle clusters which correlates with the magnetisation measurements that evidenced characteristic behaviour of magnetite. The topography and phase MFM images showed significant differences in the configuration of the magnetic domains of each material. The behaviour in relation to the Seebeck effect correlates with the structural data. From the above, we can infer that the use of pyrite as a raw material for the development of thermoelectric materials is possible given the advantages and results obtained in the present study.

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Topic: Thermoelectric Materials & Processing (MP)
Poster Presentation *P.06*

Synthesis, optical band gap and thermoelectric properties of $Sr_{1+x}TiS_{3-y}$ chalcogenide perovskites

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Inorganic chalcogenide perovskites are semiconductors with the general formula ABX_3, with A being a group II cation (i.e., Ca^{2+}, Sr^{2+}, or Ba^{2+}), B a group IV transition metal (i.e., Ti^{4+}, Zr^{4+}, or Hf^{4+}), and X a chalcogen anion (S^{2-} or Se^{2-}) [1].

Recent theoretical studies have shown that these materials may exhibit a high Seebeck coefficient and low thermal conductivity, suggesting that the chalcogenide perovskite compounds are good candidates for thermoelectric applications [2,3,4]. Some of these compounds have been poorly investigated to date. For instance, the thermoelectric data of $SrTiS_3$ have been scarcely reported, both experimental and theoretical.

Herein, we present a novel synthesis procedure to obtain $Sr_{1+x}TiS_{3-y}$ powders from the sulphuration of $SrTiO_3$ ones at different temperatures. Moreover, we show an experimental characterization of some fundamental properties of this compound that may be relevant for potential thermoelectric applications.

First, we determine the crystalline structure by x-ray powder diffraction (Figure 1 a) and electron diffraction. Tilting experiments of several crystals in the electron microscope tackled the reconstruction of the whole associated reciprocal lattice. In addition, high-resolution electron microscopy images of this compound have been acquired for the first time. Chemical composition was characterized by Energy Dispersive x-ray Analysis in a Scanning Electron Microscope. We experimentally determined the optical band gap (of about 0.96 eV) corresponding to a direct allowed transition, in agreement with previous predictions [5]. In addition, thermogravimetric analysis and differential scanning calorimetry measurements demonstrate the very high thermal stability of this perovskite (up to 700 °C in air and up to 1200°C in Argon atmosphere). Finally, we investigated the thermoelectric properties by measuring the Seebeck coefficient for samples obtained at different sulfurization temperatures (Figure 1b). There is a strong dependence of the Seebeck coefficient on the amount of sulfur vacancies, including a change from n-type to p-type behavior, as it can be seen in Figure 1c. The characteristics of the obtained chalcogenide perovskite $SrTiS_3$ may open new opportunities for the design of novel devices for high temperature thermoelectric applications.

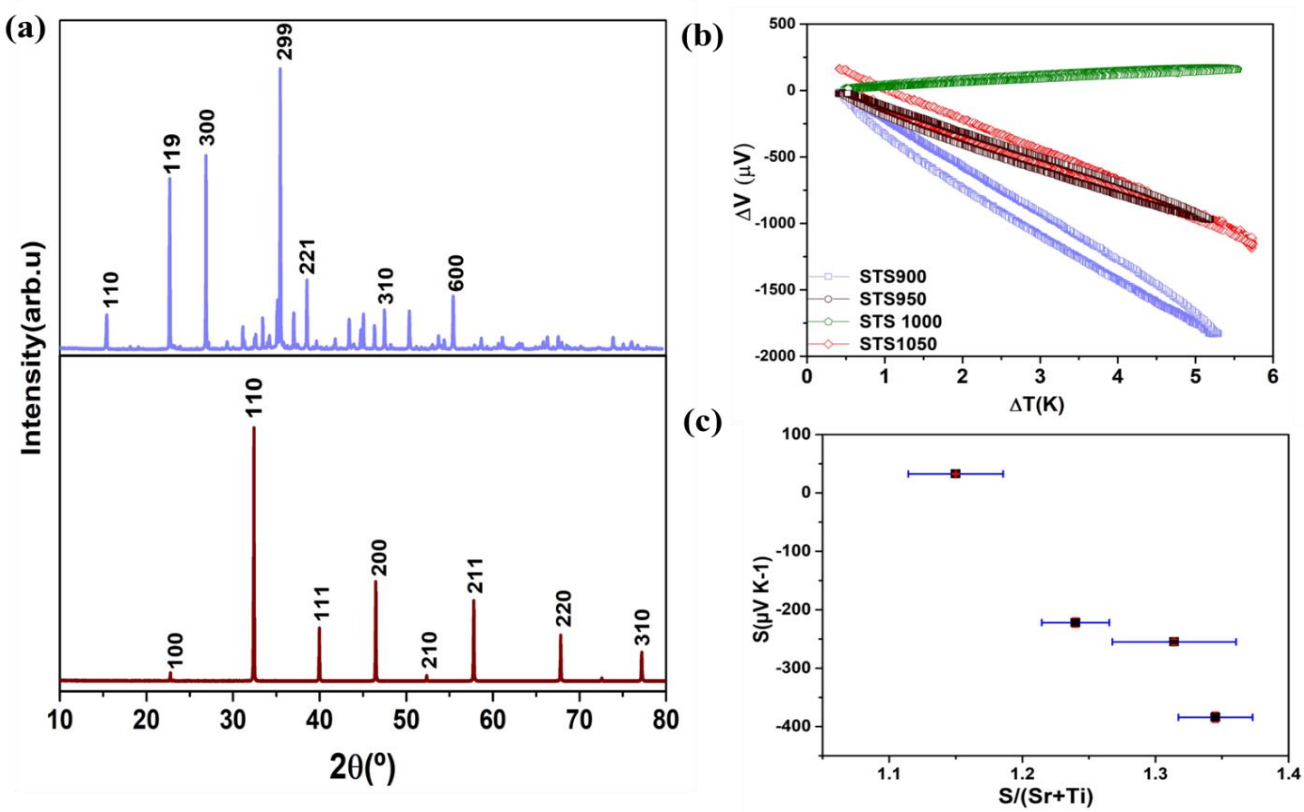

Figure 1. (a) x ray diffraction patterns of the starting $SrTiO_3$ oxide (upper panel) and $SrTiS_3$ chalcogenide (bottom panel). Miller indexes of the main diffraction peaks are indicated. (b) Thermoelectric voltage (ΔV) as a function of the temperature difference (ΔT) along the $Sr_{x+1}TiS_{3-y}$ pellets recorded during a warming up and cooling down cycle. (c) Seebeck coefficient as a function of the S/(Sr+Ti) ratio in the samples.

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Topic: Thermoelectric Devices & Applications (DA)
Poster Presentation *P.07*

Maximizing exhaust heat utilization in light- and heavy-duty driving cycles through phase-change: Simulations and Experimental validation

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The increasing electrification degree in urban mobility seems now an irreversible trend. However, the internal combustion engine seems to be far from dead, even considering the long-term goal of going towards the decarbonization of the economy. The use of sustainable fuels is an effective way of minimizing global life-cycle impact even below current battery electric vehicles (BEVs) [1]. Full vehicle electrification is still not viable for heavy duty vehicles (HDVs). Finally, current vehicles must comply with emissions standards that are impossible to attain without some degree of hybridization and efficiency-oriented strategies [1]. For these reasons, on-board electricity generation from exhaust heat seems especially attractive for the next few decades. In fact, growing vehicle electrification levels favours this approach, especially when long, high load driving cycles are frequent. This is the case of HDVs and hybrid (HEV) or plug-in hybrid vehicles used for frequent long distances, as is the case of a lot of corporate fleets.

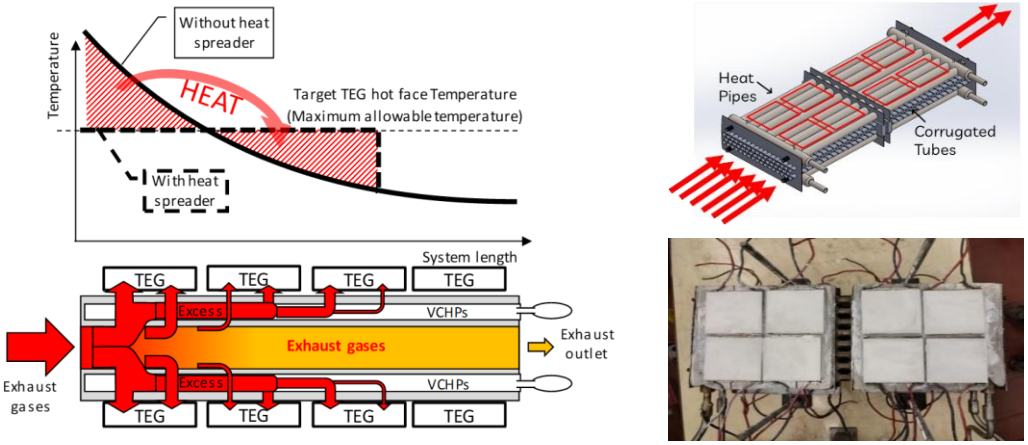
Thermoelectric generators (TEGs) would seem to be especially suited for this task given their simplicity and low maintenance needs when properly designed. However, most systems developed so far have failed to be viable, namely for cost and performance reasons.

Recent advances in affordable TE materials such as the tetrahedrite-silicide TEGs explored by the authors [2] may address the cost issue. Additionally, the authors have been exploring ways of thermally optimizing the TEG for maximum use of the available, highly variable exhaust heat of real-world driving. This included optimizing heat absorption at the exhaust, its delivery to the hot side of the TEG at an optimized level irrespective of engine regime, and its efficient removal at the cold side of the TEG [3]. An ongoing project (COOLSPOT) is dedicated to the latter part through the use of microchannels and surface modification with laser ablation.

The authors have been researching temperature controlled thermoelectric generators (TCTGs). One of the concepts is illustrated in Fig 1. It consists of using chambers located along the heat path, between the exhaust heat absorption surface and the TE modules. These chambers contain a non-condensable gas (NCG) and a working fluid that vaporizes only when close to the optimal TEG hot side temperature. This way, whenever a region of the TEG reaches this temperature, the working fluid starts absorbing heat by boiling preventing further temperature rise. Subsequently, this heat is released to under-heated regions of the system by condensation. This way, not only overheating is avoided, but also the available exhaust heat is optimally distributed along the various TE modules. This allows designing low thermal resistance heat exchangers to maximize exhaust heat absorption, without overheating risk under high engine loads, or thermal dilution under low engine loads.

The potential of the TCTG concept was illustrated in previous publications, with peak/average outputs exceeding 1.5/0.25 kW in a light duty vehicle under the WLTC driving cycle [3] and 5/2.4 kW in a HDV vehicle under a Long Haul cycle [4]. However, experimental evidence of the effectiveness of the TCTG concept had not been presented until recently. The present study illustrates both theoretically, as well as experimentally, that the proposed concept works similar to expected. Fig 1b shows two of the downsized proof-of-concept prototypes tested, which incorporate stainless steel corrugated pipes for the exhaust heat absorption and copper (MK1)

or stainless steel (MK2) heat pipes for the thermal control. Both were seamlessly integrated into a cast aluminium matrix on which the hot faces of 16 commercial BiTe modules were attached.



(a) (b)

Fig. 1. - TCTG concept (a) and experimental implementation in two proof-of-concept prototypes

The experimental results obtained with the downsized MK2 prototype attached to a 1.6L gasoline engine exhaust are presented in Fig 2. They concern the hot face temperature of the four rows of modules seen before in Fig 1b, globally validating the thermal spreading and temperature stabilization effect. The corresponding output power seen in Fig 2b exceeded 300 W for this downsized system, which is about a quarter of the size of a full system.

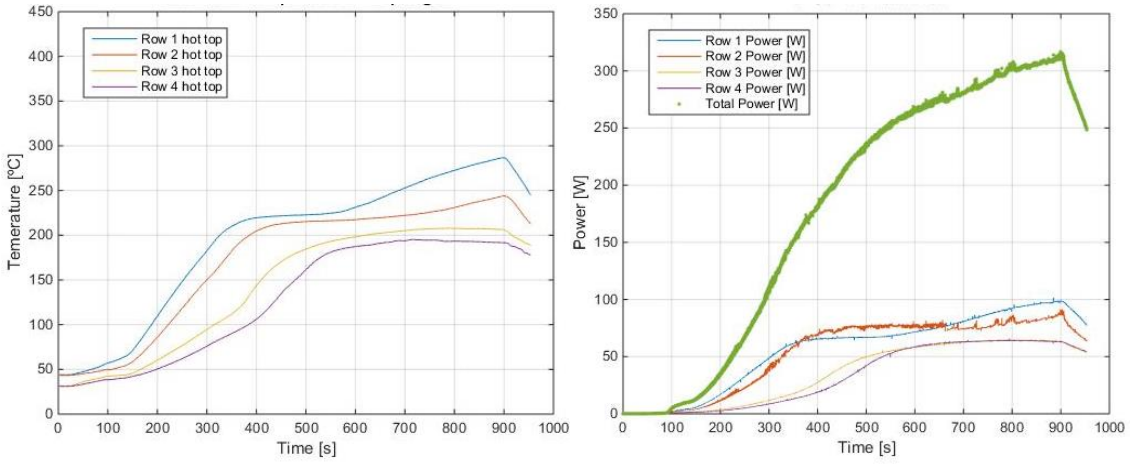


Fig. 2. MK2 prototype experimental results regarding hot face temperature (a) and output power (b).

The present results, once combined with newly developed efficient and affordable TE materials, seem to be highly promising towards the viability of vehicle TEGs.

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Topic: Other Topics on Thermoelectricity
Poster Presentation *P.08*

Soft Thermoelectric Materials: Design of 3D Printed Hydrogels

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The use of thermoelectric generators (TEG) is a viable method that allows direct conversion of heat into electricity. Although their efficiency is low, they have the advantage of low maintenance because no moving parts are required. Among the different thermoelectric compounds, organics-based materials show additional advantages such as the possibility to design flexible devices and enable the exploitation of unconventional thermoelectric effects based on species diffusion or the thermogalvanic effect [1].

This is where our materials, hydrogels, come into play. A hydrogel is a three-dimensional polymeric network that can absorb large amounts of water without dissolving in it, being a powerful platform to realize thermogalvanic cells with suitable properties such as flexibility and stability for low-grade waste heat harvesting by using abundant, inexpensive and sustainable materials [2]. In this work, soft electrolyte hydrogels with functional groups capable of anchoring the redox pair ($Fe^{3+/2+}$ and $Fe(CN)_6^{4-/3-}$) have been designed, fabricated and characterized, producing an alteration of the solvation entropy of the species. These materials are prepared using an LCD-based SLA 3D Printer to obtain the shape that best fits our devices. In addition, the interaction between the different redox pairs and the hydrogels based on triazine and AETA monomer is studied by infrared spectroscopy.

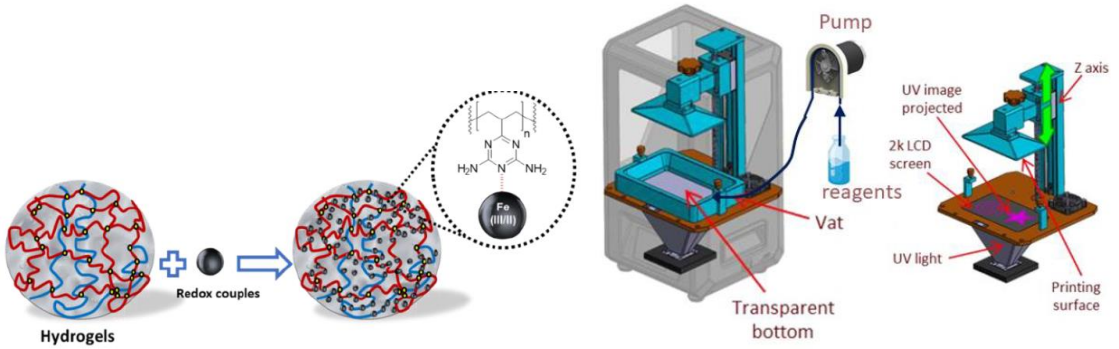

Fig. 1. (left) Coordination between the redox couple and triazine-based hydrogel. (right) SLA 3D printer.

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