Giornate Sulla Termoelettricità 2022

Book Of Abstracts

16 – 17 FEBBRAIO

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Programma

Mercoledì 16 febbraio 2022

10:00	Registrazione dei partecipanti

10:30	Benvenuto istituzionale e introduzione del presidente dell'AIT

Invited lecture

10:50	Simone Fabiano - Linköping University, Sweden *Unconventional thermoelectric materials for energy harvesting and sensing application*

Sessione 1: Thermoelectric generators and devices (I)
Chair: Francesco Rossella

11:50	Elisabetta Di Maggio - Università di Pisa *Thermoelectric devices based on nanostructured silicon, the ideal material for thermoelectric applications*

12:10	Federico Giulio - Università degli Studi di Milano-Bicocca *Exceptional thermoelectric power factor in hyperdoped, fully dehydrogenated nanocrystalline silicon thin film*

12:30	Valeria Demontis - Scuola Normale Superiore di Pisa *Drastic reduction of thermal conductivity in InAsSb periodic twinning nanowires*

12:50	Giovanni Pennelli - Università di Pisa *Electrical and thermal optimization of energy-conversion systems based on thermoelectric generators*

13:10 - 14:30	Pranzo

Sessione 2: Thermoelectric materials: design and characterization
Chair: Valeria Demontis

14:30	Cristina Artini - Università di Genova/CNR ICMATE *Effects of deposition and annealing temperature on the electrical properties of skutterudite $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ thin films*
14:50	Stefano Boldrini - CNR ICMATE *Ultrafast sintering of Mg_2Si*
15:10	Alessandro di Falco - Università di Torino *Half-metallicity, itinerant magnetism and electronic properties of Co_2ZrSn and Co_2HfSn Heusler alloys: an experimental and ab-initio combined study*
15:30	Antonella Rizzo - ENEA, Brindisi Research Centre *Al:ZnO-based thin films: a thermoelectric material for room temperature applications* Francesca di Benedetto/Antonella Rizzo - ENEA, Brindisi Research Centre *Comparative study on the thermoelectric properties of p-type CuI thin films*
16:00 - 16:25	Coffee break

Sessione 3: Thermoelectrics in enterprise applications
Chair: Valeria Demontis

16:25	Bruno Lorenzi - GemaTEG Italia Srl, Perugia *Cogeneration by a plug-in thermoelectric device integrated within a conventional solar-thermal system*
16:45	Fabio Puglia - ISC_Oversonic srl *Application of thermoelectric tegs to functional safety systems of anthropomorphic robots*

17:05	Assemblea dei soci dell'AIT

20:00	Cena Sociale

Giovedì 17 febbraio 2022

Sessione 4: Computational approaches to materials design and investigation
Chair: Simone Fabiano

10:00	Dario Narducci - Università degli Studi di Milano-Bicocca *Strange Thermoelectrics*

10:20	Eleonora Ascrizzi - Università di Torino *Ab initio study of bulk and defective ZrNiSn half-Heusler alloys*

10:40	Alberto Castellero - Università di Torino *Role of defects and secondary phases on the electronic structure and transport properties of thermoelectric $TiNi_{1-x}Sn$ half-Heusler*

11:00	Paolo Sebastiano Floris - Institut de Ciència de Materials de Barcelona, Spain *Impact of doping on the thermal conductivity of PEDOT and PEDOT:PSS through Molecular Dynamics simulations*

11:20	Coffee break

11:40	Patrizio Graziosi - CNR ISMN *ElecTra: A Botzmann Electronic Tranport simulator for complex bandstructure thermoelectric materials*

12:00	Himanshu Nautiyal - Università di Trento *First principles investigation of transport properties of 2D SnX2 (X=S, Se) and Janus SnSSe monolayer*

12:20 - 14:00	Foto di gruppo nella scalinata del Palazzo della Carovana e
14:00	Binayak Mukherjee - Università di Trento *Topological Anderson Insulator in Cation-Disordered Cu2ZnSnS4*

Sessione 5: Thermoelectric generators and devices (II)
Chair: Dario Narducci

14:20	Ketan Lohani - Università di Trento *Facile and low-cost fabrication of Cu/Zn/Sn-based ternary and quaternary chalcogenides thermoelectric generators*
14:40	Caterina La Terra - Politecnico di Milano *Modelling and characterization of thermal transfer in a thermoelectric generator based on catalytic combustion*
15:00	Discussione su collaborazioni, progetti e prossime conferenze nel campo della termoelettricità (Coordina: Dario Narducci)
16:30	Fine della Conferenza

Contributi

INVITED LECTURE

Unconventional thermoelectric materials for energy harvesting and sensing applications

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Traditional solid-state inorganic semiconductors have dominated the research stage on thermal-to-electrical energy conversion. Still, they face several challenges connected to the scaling up of material synthesis and the high cost of the raw materials. Carbon-based semiconductors have recently emerged as potential thermoelectric materials for low-temperature energy harvesting, primarily driven by the high abundance of their atomic elements, ease of processing/manufacturing, and intrinsically low thermal conductivity. This quest for new materials has resulted in the discovery of several new kinds of thermoelectric materials and concepts capable of converting a heat flux into an electrical current through various types of particles transporting the electric charge: (i) electrons, (ii) ions, and (iii) redox molecules. This has also contributed to expanding the applications envisaged for thermoelectric materials far beyond the simple conversion of heat into electricity. Here, I will summarize our effort to develop efficient ionic and electronic conducting polymers. I will discuss strategies to maximize the thermal-to-electrical energy conversion efficiency of printed organic thermoelectric modules and present case studies highlighting the potential of ionic and electronic conductors for unconventional energy harvesting and sensing applications.

SESSIONE 1: Thermoelectric generators and devices (I)

Chair: Francesco Rossella

Thermoelectric devices based on nanostructured silicon, the ideal material for thermoelectric applications

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Silicon is a material largely available, biocompatible and technically feasible; for this reason, it has become the prince material for device fabrication, and it is at the base of the electronic industries, which offer an important technological issue making available a huge amount of capabilities for doping, contacts, etching, lithography and so on. Between all the advantages of silicon as a material, it has also a very high power factor, which can reach, with a suitable tailoring of the doping concentration, values of 5×10^{-3} W/(m K^2) at room temperature. This, combined with the reduced thermal conductivity when nanostructured, results in a very high figure of merit. Moreover, silicon is very stable in a large range of temperatures, in excess of 900 K. Extrapolating the few experimental data available in literature, it can be shown that *ZT* increases with temperature, reaching values of *ZT*>5 at 900 K[1], when the thermal conductivity is reduced below 2 W/(m K). Such a low thermal conductivity has been measured, at room temperature, in large arrays of vertical silicon nanowires[2,3].

The crucial point is to develop technologies for the reliable and low-cost fabrication of large collections of interconnected silicon nanostructures, with processes that can be compatible with standard industrial techniques. Techniques based on metal-assisted etching[4] allow the fabrication of large arrays of silicon nanowires, perpendicular to a silicon substrate, which can be contacted by metal electrodeposition[5]. These techniques are low cost, can be applied to large areas, and could be implemented in production lines similar to that of photovoltaic panels, for large scale applications of energy harvesting.

The technological feasibility of silicon and, in particular, the available high resolution lithographic techniques can be exploited for the fabrication of integrated micro-generators based on suspended nanostructures. These micro-devices can be fabricated side-by-side with conventional electronic circuits which could exploit a hot surface for their supply: battery-free systems, such as sensor nodes or devices for IoT, can be envisaged.

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Exceptional thermoelectric power factor in hyperdoped, fully dehydrogenated nanocrystalline silicon thin film

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Boron hyperdoped nanocrystalline silicon (nc-Si) was reported to show an enhancement of the thermoelectric power factor (PF) after a thermal treatment (TT) at T ≥ 800°C for 2 hours in Ar as a result of the simultaneous increase of the Seebeck coefficient and of the electrical conductivity[1,2]. This increase is due to energy filtering (EF) occurring at the grain boundaries (GBs) of the material after the precipitation of SiB_x at GBs[3]. However, PFs enhancement was also found to depend on the size and aging of the samples. Aim of this communication is to show how this behaviour is related to the presence of hydrogen in nc-Si.

Hydrogen is embedded in nc-Si films during the CVD process (from SiH_4) and can complex the boron[4] interfering with the formation of SiB_x precipitates and then hindering the formation of the potential barriers needed to enable EF. As an alternative, hydrogen might compete with boron at decorating the GBs, hampering its localized precipitation.

To verify this hypothesis, following Solvoy *et al.*[5] we stipulated that the removal of hydrogen by annealing is sensitive to the capability of Ar to prevent the formation of a stagnating H_2 layer at film surface. For any given Ar flux, this is shown to depend on the sample size, preventing the complete outdiffusion of H_2 in large samples. Without hydrogen more boron is available for the formation of SiB_x precipitates with a consequent enhancement of the PFs.

To check this hypothesis large samples were submitted to a TT at 1000°C for 2 hours under a tripled Ar flux. We found that the PFs of the small and large samples aligned to each other suppressing the size effect.

Hydrogen also let explain aging. In aged sample hydrogen had time to leave the films under static conditions and at room temperature independently of the samples size. This explains why TT of aged, fully dehydrogenated samples leads to gigantic PFs. We will show how a full dehydrogenation of samples could lead to a PF of 31 mW/K^2m which, for a thermal conductivity[6] of 10 W/mK for nc-Si with grains size of 50nm, would lead to a ZT of ~0.9 at 300K.

Bibliography:
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Drastic reduction of thermal conductivity in InAsSb periodic twinning nanowires

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We experimentally demonstrate a one order of magnitude reduction of thermal conductivity in InAsSb NWs thanks to the periodic repetition of twin planes defects along the NW axis [1]. The growth of such NWs, referred to as twinning superlattices (TSL) NWs, is obtained by finely tuning the growth parameters, the NW diameter and by introducing controlled amounts of impurities, i.e. small amounts of Sb in InAs NWs [2]. InAsSb TSL NWs with different period of repetition of the twin planes were used to fabricate suspended NW devices allowing to measure the thermal conductivity, k, exploiting the 3-omega technique [3,4], and the results of the combined electrical and thermal study are compared with the results achieved in twin-free crystal NWs. The outcomes reveal a factor 10 reduction of k while maintaining unaltered electrical transport properties, corresponding to a factor 10 increase of the estimated thermoelectric figure of merit ZT (approximately from 0.02 to 0.2), and highlighting the strong potential for TSL NWs as a novel platform for high-performance thermoelectric harvesters.
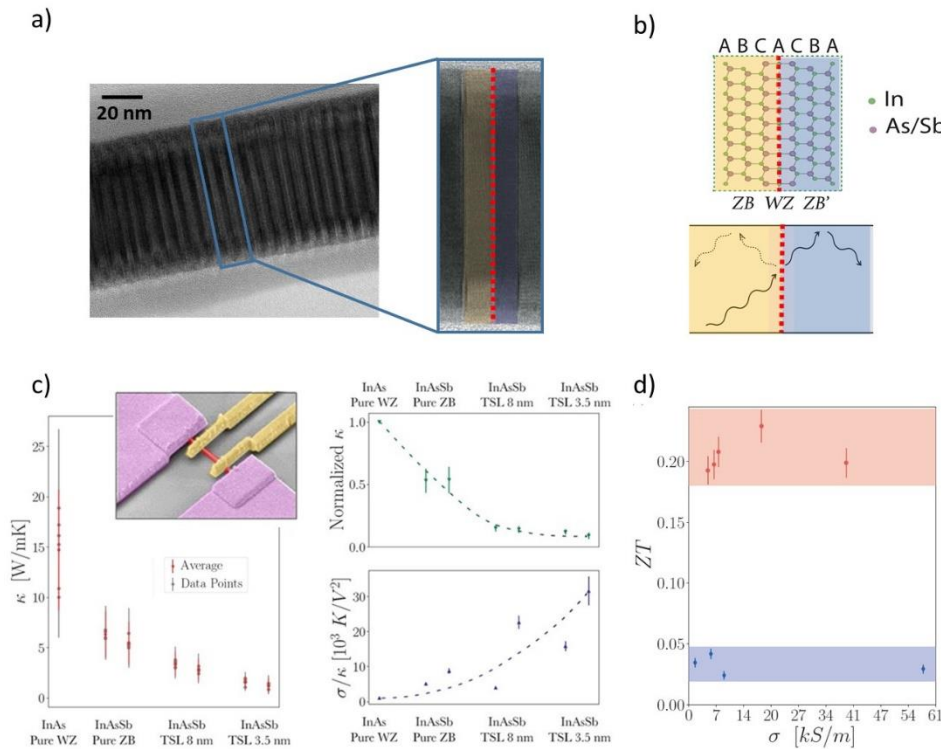
Figure 1:a) HRTEM of a TSL InAsSb NW; b) ball-stick representation of a TSL InAsSb NW and schematic depiction of the phonon scattering mechanisms; c) measured thermal conductivity and $\frac{\sigma}{k}$ ratio (the inset in the upper-right part of the graph shows a SEM image of the fabricated device); d) comparison of the estimated thermoelectric figure of merit ZT for pure crystal InAsSb NWs (blue part) and TSL InAsSb NWs samples (red part).

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Electrical and thermal optimization of energy-coversion systems based on thermoelectric generators

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Thermoelectric devices are very attractive for a large variety of applications of energy scavenging and green energy harvesting, and they can also be been used for cooling, in particular in those applications in which a localized control of temperature is required. Highly efficient thermoelectric devices require, at first, the development of performing materials with high Seebeck coefficient and electrical conductivity, and low thermal conductivity. However, although the selection of materials with good thermoelectric performances is fundamental, the development of strategies for the optimization of the geometrical factors of the device and of the thermal coupling, as well as the optimization of the electrical power output, are required for an optimal exploitation of heat sources.

We have developed a model based on an equivalent electrical circuit[1], which takes into account both the electrical part, comprehensive of the electrical power conditionig circuit, and the thermal part, including the coupling with the heat sources. This equivalent model can be applied to the optimized design of systems for both thermoelectric generation and thermoelectric cooling.

We will show that the model yields valid results when applied to ideal thermoelectric generators, with either ideal or non-ideal heat exchanges. In realistic thermoelectric conversion systems, the model gives a correct description of the effect of thermal contact resistances, and it can be used to achieve the correct matching both of the electrical load and of the thermal coupling with the heat sources.

In particular, considerations on the maximum power output and maximum efficiency power management strategies[2] will be reported and quantitatively compared, and it will be shown how the model can be applied for the correct design of the electrical load, through the control strategy of the DC/DC converter.

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SESSIONE 2: Thermoelectric materials: design and characterization

Chair: Valeria Demontis

Effects of deposion and annealing temperature on the electrical properties of skutterudite $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ thin films

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Filled skutterudites are promising thermoelectric materials thanks to their high power factor and low thermal conductivity [1,2]. The reduction of the latter, in particular, can be improved by adding scattering centers, for instance by inserting filling ions, or by lowering dimensionality. With the aim to optimize the thermoelectric properties of the $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ filled skutterudite, thin films belonging to this system were deposited under vacuum conditions by the pulsed laser deposition (PLD) method on fused silica substrates at room and at high (423 K) temperature [3], and subsequently annealed. XRD analyses suggest that only annealed films present a highly crystalline skutterudite not accompanied by extra phases; accordingly, transport property values become stable only after three thermal cycles up to 523 K, thus highlighting the importance of the annealing process. With reference to the transport properties of annealed films, electrical conductivity assumes values higher than the ones of bulk samples [4], while the Seebeck coefficient results to be far lower, thus determining lower values of the power factor. Room temperature thermal conductivity is similar in Sm-doped films and in (Gd,Sm)-doped bulk samples [5], suggesting that the presence of interfaces in films acts similarly to the introduction of different filler ions in bulk samples. The annealing process also causes the reduction of both carriers' concentration and their mobility.

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Ultrafast sintering of Mg$_2$Si

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Sintering is the traditional way to produce bulk materials partially inheriting powders nanostructure. Recently a rapid pressure-less technique has been proposed [1], Ultrafast High-temperature Sintering (UHS), able to produce (sometime to synthesize) a large set of ceramics, metals and intermetallics within tens of seconds. Among the advantages of this technique, there are the unprecedented versatility and control on the grain growth and the possibility to scale down by two order of magnitude both the time (and energy consumption) for sintering and the experimental setup cost. In this presentation possibly the first application of this technique to a thermoelectric material, Mg$_2$Si, is presented.

Despite the relatively low sintering temperature used and the consequently relatively slow heating rate ($\sim 10^2$ °C/s, near the lower limit for UHS), samples with good mechanical properties were typically produced with ≤ 1 minute holding time.

The complete elimination of the nanostructured porosity was not possible for this material, in analogy with the findings of pressure-less Spark Plasma Sintering (SPS) [2]. The role of this porosity is discussed in light of the morphology and composition analysis (SEM – EDS), thermal conductivity (Laser Flash Analysis) and electrical properties (conductivity and thermopower), and the obtained properties compared to conventionally (pressure assisted) SPS results. Sintering process effectivity for Bi-doping was studied by solid state 29Si MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) and electrical measurements.

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Half-metallicity, itinerant magnetism and electronic properties of Co_2ZrSn and Co_2HfSn Heusler alloys: an experimental and ab-initio combined study

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Half-metallic ferromagnetic alloys are attracting considerable interest for their potential applications in spintronic devices. Since the development of spin-voltage generators is regarded as crucial in spintronics, thermoelectric properties are also of high interest for such technology, having been proved spin-Seebeck effect to be an effective way to generate and carry spin-polarized current over relatively long distances. Therefore, half-metallic alloys which show a constant, relatively large Seebeck coefficient (when compared with other thermoelectric materials) and a high Curie temperature (possibly above room temperature) are greatly looked after. Co-based Heusler alloys are considered to be among the most promising classes of half-metallic compounds as they combine suitable magnetic, electronic and transport properties with compositional versatility and high thermal stability. Also, several Co-based Heusler alloys were found to be suitable for spin-injection processes due to their semiconductive-like band gap located in one of the two electronic sub-bands, and progressively became the focus for prospective spintronic devices operating close to room temperature.

In this work, Co_2ZrSn and Co_2HfSn Heusler alloys were studied by combining experimental and ab-initio investigations in order to accurately estimate their electronic density of states in proximity of the Fermi level and to determine their half-metallic, magnetic and electronic properties. Magnetization measurements showed for both alloys a gradual transition from half-metallic ferromagnetism to weak itinerant ferromagnetism with increasing temperature, well described by a simple mean field model up to the Curie temperature and beyond. Ab-initio calculations were performed using two exchange-correlational functionals, PBE and PBE optimized for solids (PBEsol), in order to assess the reproducibility of theoretical results. Overall, band structures and density of states diagrams indicated, for both compounds, the presence of a half-metallic band gap in the minority spin sub-band. The Half-metallic behaviour of both alloys was confirmed by the observation of a peculiar trend of magnetization as a function of temperature, which is linked to a shift of spin-flip mechanism as the thermal contribution increases. The profiles of Seebeck coefficient and Power Factor as a function of temperature are unusual, presenting a linear growth below the Curie point, followed by a flat plateau beyond.

Al:ZnO-based thin films: a thermoelectric material for room temperature applications

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Al:ZnO (AZO) is a very interesting transparent n-type thermoelectric materials. If coupled with suitable transparent p-type thermoelectric material it could open the way to the realization of a transparent thermoelectric generator (TEG).

Al-doped ZnO thin films were deposited using a RF magnetron sputtering system in $Ar+O_2$ atmosphere by co-sputtering method with two distinct targets (ZnO and Al), where the Al percentage was varied changing the power ratio between the two targets from 0.1 to 0.7.

Optical emissions (EOS) from the plasma during the deposition were measured using a high resolution spectrometer in the wavelength range of 360-800 nm. EOS show that the constituents of each target were successfully sputtered off. A plasma emission spectrum shows the presence of Zn+, Zn, Al and O emission lines. The Zn and Al concentrations in the plasma can be calculated and correlated to Al:ZnO thin films properties.

The structural properties of the realized films were characterized by X-ray diffraction measurements performed under glancing incidence conditions.

Thermoelectrical and electrical characterizations were conducted in order to compare the response of films grown under different conditions, using both specific chips as substrates for a Thin Film Analyzer characterization – based on hot stripe method on suspended membrane – and glass substrates for a more standard Van der Pauw configuration of measurement.

Optimal procedures were adopted to gain repeatability, accuracy and a better control of the systematic errors. All measurements were performed in the temperature range of 20-50°C. The future efforts will be devoted to pull up the temperature edge of characterization to prove stability of thin film performances.

Comparative study on the thermoelectric properties of p-type CuI thin films

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Over the past few years, efforts have been made to develop new thermoelectric materials based on earth-abundant, non-toxic and low-cost elements in order to boost the adoption of the thermoelectric technology and foster its large-scale application. Copper iodide (CuI) is a material of recent interest for thin film thermoelectric applications because it is a p-type candidate with performance equivalent to the currently in market n-type material in term of optical transparency and electrical conductivity.

In this work we reported a comparative study on the thermoelectric properties of CuI thin films obtained by physical evaporation of CuI commercial precursor - with or without subsequent iodination - or direct iodination of Cu thin layers.

All the thin films were characterized to study the morphology, structure and chemical aspect of the realized CuI thin films. Particular attention was focused on the thermoelectric, thermal and electrical characteristics of the realized samples deposited onto pre structured chip and bare substrates by using a thin film analyzer (TFA) equipped with HCS1 module.

SESSIONE 3: Thermoelectrics in enterprise applications

Chair: Valeria Demontis

Cogeneration by a plug-in thermoelectric device integrated within a conventional solar-thermal system

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Low conversion efficiency and cost are the leading causes of thermoelectric generators' limited presence in the marketplace. Integration in commercially viable solutions tailored to specific niches may address the limitation of this technology, opening new opportunities in energy harvesting from renewable sources. GemaTEG has developed an innovative plug-in device for cogeneration within a conventional thermal solar panel. The system consists of vacuum tubes with thermosyphon able to harvest solar energy, and store it in a dedicated reservoir though a heat transfer fluid. A thermoelectric harvesting chamber between the thermosyphon condenser and the heat transfer fluid allows cogeneration of heat and electricity without the complexity of moving parts.

The following presentation shares the methodology adopted for the system optimization, the experimental data from the prototype, and several opportunities for improvement currently under evaluation. An electrical conversion efficiency around 4% is within reach with commercial Bi_2Te_3 modules and optimized thermosyphon configuration. Larger conversion efficiency requires more invasive approaches to increase the absorber surface and minimize the loss while maintaining the system static (without tracking devices). Furthermore, opportunities for cogeneration after sunset may further increase the benefits.

APPLICATION OF THERMOELECTRIC TEGS TO FUNCTIONAL SAFETY SYSTEMS OF ANTHROPOMORPHIC ROBOTS

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In the context of the technological nowadays scenario, collaborative and anthropomorphic robotics mainly, is increasingly assuming an operational role and effectiveness in supporting man in activities that are not completely codified or replacing them in dangerous and tiring jobs. For this reason, ISC-Oversonic started at the end of 2020 a Humanoid Robotics Project that is gaining increasing interest. One of the main issues related to the management of the RoBee System is the management of thermal flows, dissipation and power supply of safety sensors on board. In this last application slot, the use of thermoelectric technologies can be strategic to continuously power the local safety sensors in accordance with EN ISO 13849-1 and EN ISO 13849-2. The challenge is therefore to propose TEG as a certified element of functional safety in advanced cobot systems.

The humanoid system is powered by 48V DC and has within it multiple electronic calculations mainly responsible for computer vision and training of neural networks in edge-computing. The covering *suit,* made of particular fibers to allow effective thermal insulation and to make the system completely waterproof with IPX4 degree while determining critical issues in the management of thermal flows, defines the operating envelope. The presentation therefore aims to show the operating conditions, the safety of the *safe mode* (SIL 3 compliant to EN 60204-1) in the phases of human-machine interaction, and how thermoelectric is used. In detail, the results of both the analytical simulations and the FEM analysis will be presented. The TEGs were applied during the tests both using classic and flexible modules with different temperatures range and heat exchanger characteristics. Heat decentralization was managed through specially designed heat-pipes.
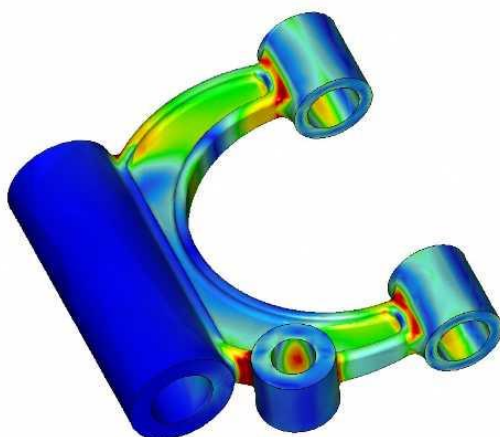
SESSIONE 4: Computational approaches to materials design and investigation

Chair: Simone Fabiano

Strange Thermoelectrics

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In addition to its most widespread metrologic application, thermoelectricity is commonly seen as a tool either to convert heat into electric power or, conversely, to extract heat from a sink. This has somehow concentrated research effort toward materials with high figures of merit according to the celebrated paradigm of the electronic conductor – phononic glass. However, over the last years more exotic applications of thermoelectricity have surfaced, in no way connected either to energy or temperature measurements [1]. In this talk I will address a few of such 'strange applications', which could contribute to further extend the interest toward thermoelectricity. Two study cases will be specifically considered, connected to electrocatalysis and to chemical sensing.

Use of Seebeck effect to modify (improve) the catalytic activity of oxides have been reported by Huang and coworkers [2]. The basic idea is to induce a shift of the Fermi level at the catalytic surface by applying a controlled heat flux across the thermoelectric catalyst. In this way, electronic exchange responsible for promoting a reaction at the surface is obtained. The effect is fully equivalent to that obtained by applying an electric polarization across the catalyst, with the remarkable advantage of not needing porous electric contacts to be deposited on the outer surface. Ideal thermoelectric catalysts are therefore materials showing a large Seebeck coefficient and a low thermal conductivity – with no additional constraint on their electrical conductivity. The approach has already found preliminary applications to hydrogenate CO_2 [2] and to produce hydrogen peroxide [3].

A similar use of the Seebeck effect may be conceived for chemical sensors. In chemoresistive devices, it is well known how sensitivity is seldom an issue, while the real challenge is selectivity. The standard approach to overcome the problem is to build up a matrix of sensors, feeding its response to some numerical device (e.g. a neural network). A single chemical sensor may be used, instead, where the Fermi energy is swept by modifying the temperature drop across it. A spectrum of its (electrical) response as a function of Fermi energy is then obtained, witnessing its changing catalytic activity toward the oxidation/reduction of the analyte. Applications of the so-called Seebeck sensors (not to be confused with the gas sensors powered by TEGs) have been obtained, among others, to selectively detect hydrogen [4, 5] – quite a sensitive issue in view of the many uses of hydrogen both as an energy vector and for energy storage.

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Ab initio study of bulk and defective ZrNiSn half-Heusler alloys

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In recent years, thermoelectric (TE) materials have become of increasing interest, thanks to their electronic and transport properties which make them very suitable as green energy sources. Among different TE materials, the half-Heusler (HH) alloys are of particular interest for their excellent electronic transport properties and their tunable band gap, which allow the possibility of tailoring TE efficiency.[1] The presence of defects can enhance TE properties of alloys, but from an experimental point of view it is always very difficult to establish the exact relationship between properties and atomic structure. This knowledge would be of great importance, since it provides an indication on how to improve the performances of thermoelectric materials. In this framework, ab initio study and characterizations of TE materials can help to detect, evaluate and improve thermoelectric properties, by analyzing the bulk structure and the role of defects in modifying the electrical conductivity and transport properties. While TiNiSn-based alloys are now known as reliable thermoelectric materials,[2] there are still few experimental measurements on ZrNiSn-based alloys, even though their Seebeck coefficients were found to be higher than in the TiNiSn compounds.[3] At the same time, when these materials are used in the TE generator devices, not only their thermoelectric properties, but also their thermal stability is very important. ZrNiSn has good properties also in this respect, with a thermal stability higher than TiNiSn.[4, 5] Considering these promising features, we turned our attention to an ab initio characterization of ZrNiSn-based alloys with the CRYSTAL code,[6] using DFT-PBE calculations and basis sets of localized Gaussian orbitals. The obtained structural, electronic and thermoelectric properties for the pristine ZrNiSn alloy are in good agreement with those reported in experimental studies, revealing a higher computed power factor with respect to TiNiSn. Then, in order to build models consistent with experimental samples,[7, 8, 9] three of the most likely point defects were simulated: (1) an interstitial Ni atom, (2) an antisite and (3) a Sn/Sb substitution (see Fig. 1). The effect of these defects on the electronic properties has been evaluated through the calculation of band structures and density of states. Both the interstitial Ni and the antisite defect introduce states in the forbidden energy region, reducing the band gap and even causing the system to be metallic if the defect concentration is high enough. The band structure of the Sb-doped supercell shows a shift of the Fermi level toward the conduction band. This could lead to a possible increase of the carrier concentration, σ and ZT. The transport properties calculated for the defective systems will be shown, compared and commented, with the aim of clarifying the different mechanisms and proposing the design of increasingly performing materials.
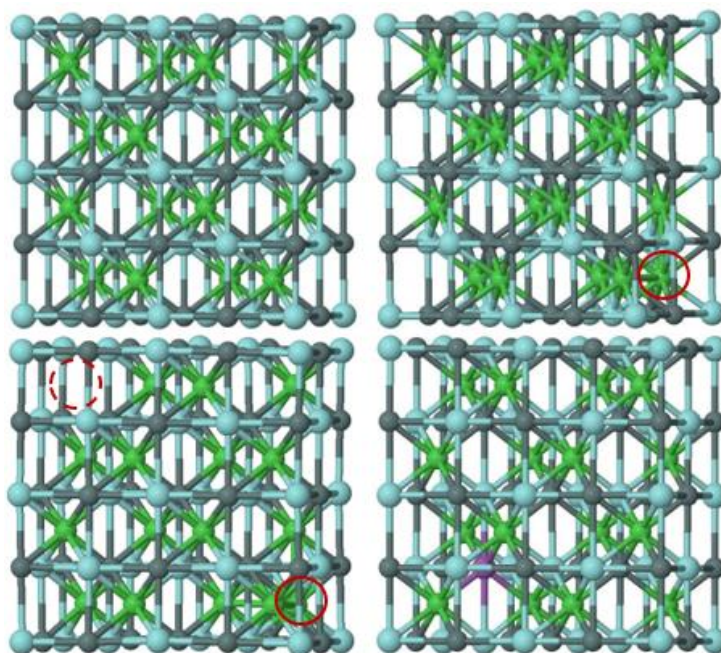
Fig.1. Optimized structures of 2x2x1 ZrNiSn bulk and defective supercells. Pristine ZrNiSn (upper right panel), interstitial Ni defect highlighted with a red circle (upper left panel), anti-structural defect: a red circle highlights the interstitial Ni atom and a dashed red circle the vacancy (lower right panel), substitutional defect: a Sn atom is substituted with a Sb atom, represented with a purple sphere (lower left panel). Green spheres represent Ni atoms, cyan represent Zr atoms and gray represent Sn.

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Role of defects and secondary phases on the electronic structure and transport properties of thermoelectric TiNi$_{1+x}$Sn half Heusler compounds

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The MNiSn (M = Ti, Zr, Hf) alloys were among the first half Heusler compounds to be characterized in terms of thermoelectric properties (i.e., electrical resistivity and Seebeck coefficient). Since then, this family of compounds has been extensively studied both from the experimental and computational point of view, leading to the development of high performing thermoelectric materials (ZT$_{max}$ = 1.5 at 820 K) such as Ti$_{0.5}$Zr$_{0.25}$Hf$_{0.25}$NiSn. Among half Heusler compounds TiNiSn is considered a model system for understanding the relationship between structural, microstructural and thermoelectric properties. According to the ternary phase diagram, the formation of TiNiSn half Heusler single phase from the melt is hindered by a complex solidification path and requires long annealing time. A literature survey shows that different samples of nominally stoichiometric TiNiSn have extremely scattered values of electrical conductivity and Seebeck coefficient. Such a dispersion of data can be ascribed to residual secondary phases and point defects, that affect the charge carrier concentration. On the one hand, the presence of metallic secondary phases (e.g. TiNi$_2$Sn, Ni$_3$Sn$_4$, Ti$_6$Sn$_5$, Sn) increases the charge carrier concentration in the sample, raising the electrical conductivity and lowering the absolute value of the Seebeck coefficient. On the other hand, point defects act as intrinsic dopants and their role on the electronic and thermoelectric properties was investigated both experimentally and theoretically several authors. It was demonstrated that a small excess of Ni leads to the partial occupancy of the Wyckoff position 4d (interstitial Ni defect) expanding the cell, without precipitation of the full Heusler compound TiNi$_2$Sn due to the slight solubility of TiNiSn for Ni.

The above picture shows that, at the current stage, the understanding and control of both the role and concentration of defects that deviate from the ideal crystal is far from complete. In this view, the aim of this work is twofold. On the one hand, we investigate the role of punctual defects on the thermoelectric properties of TiNiSn through DFT modelling. On the other hand, we compare the calculated thermoelectric properties with the experimental values obtained for TiNi$_{1+x}$Sn samples in bulk form.

DFT calculations showed that the presence of both interstitial Ni defects and composition conserving defects narrow the band gap with respect to the defect free structure leading to values that are comparable to the experimental one. Accordingly, experimental investigations confirmed that interstitial Ni defects, as well as metallic secondary phases, increase the metallic behaviour of the defective structure with respect to the defect free structure, raising the electrical conductivity and lowering the absolute values of the Seebeck coefficient.

Impact of doping on the thermal conductivity of PEDOT and PEDOT:PSS through Molecular Dynamics simulations

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Organic materials for thermoelectric applications have attracted a fair amount of attention in recent years due to remarkable advances achieved in terms of their *ZT* (the thermoelectric figure of merit): a value of 0.42 has been reported by [1]Kim et al. for poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) films treated with dimethyl sulfoxide (DMSO), while 0.25 has been obtained for PEDOT:Tosylate by [2]Bubnova et al. In this work we investigate various PEDOT and PEDOT:PSS samples in both their neutral and doped (bipolaronic) state and with distinct concentrations of PSS through Molecular Dynamics, by taking advantage of the all-atom force field recently developed by [3]Micheals et al. In the case of bare PEDOT we find that changing the distribution of chain lengths affects the thermal conductivity of neutral and doped samples in a different way: longer chain lengths result in higher conductivities in the neutral scenario, whereas an intermediate chain length gives the highest value in the bipolaronic case. The role of PSS and of its concentration is discussed in the bipolaronic case.

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ElecTra: A Botzmann Electronic Tranport simulator for complex bandstructure thermoelectric materials

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We introduce the open-source simulation code ElecTra (Electron Transport simulation lab), [1] which computes the transport coefficients in bipolar complex bandstructure materials within the energy and momentum dependent relaxation time approximation. We couple the Boltzmann transport method to DFT bands for half-Heusler materials, considering both electron-phonon and ionized dopant scattering. The full energy and momentum dependence of the relaxation times is essential in capturing the correct transport features. [2-4]

We then compare the conventional combination of unipolar transport coefficients with the simultaneous consideration of the full bipolar effects in the calculation of the transport coefficients. A large difference between the two treatments exists for narrow bandgap materials.

Lightly doped narrow gap semiconductors with asymmetric conduction/valence bands offer the unconventional possibility to achieve extremely high thermoelectric power factors of up to 50 mW/mK^2, if they possess highly asymmetric conduction and valence bands in terms of density of states or phonon scattering rates. This is achieved because, under these conditions, charge transport becomes phonon scattering-limited, which allows large conductivities. Finally, we interpret related experimental findings. [5,6]

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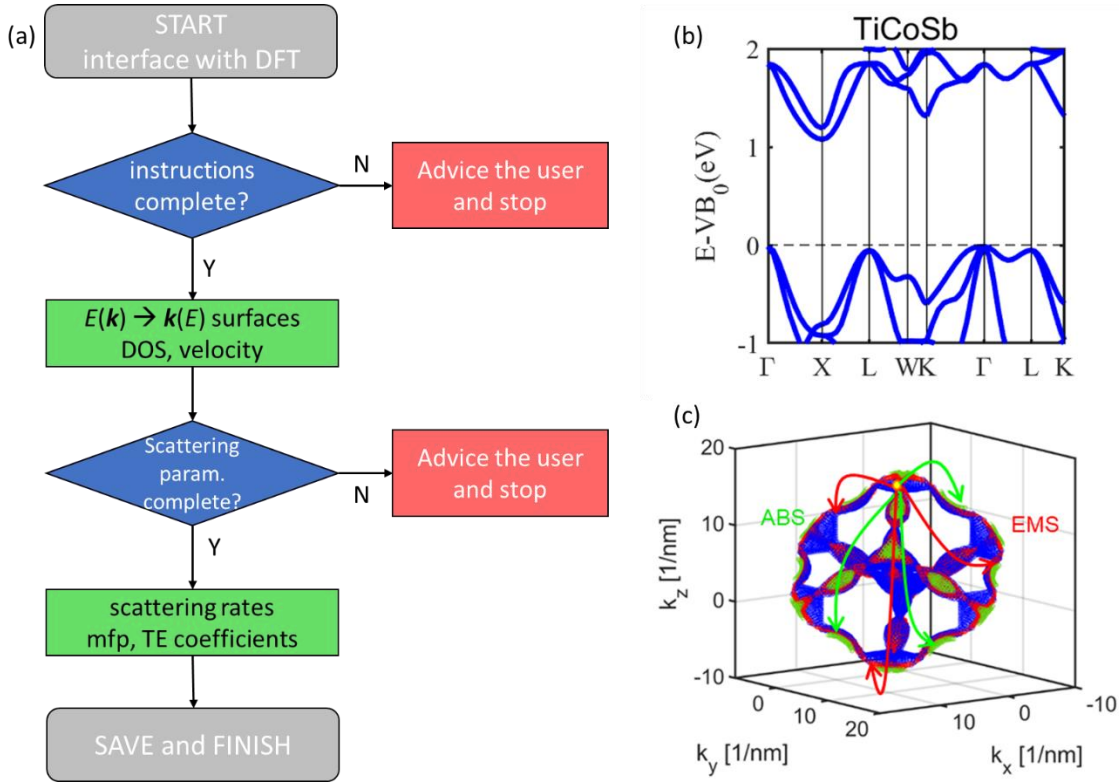
Figure1: (a) flow chart of the ElecTra code; (b) TiCoSb bandstructure; (c) constant energy surfaces from the TiCoSb valence band 0.12 eV below the band edge (blue), and other two surfaces from other band indexes at different energies, constructed by ElecTra code and represented in cartesian axes to compute the tensor components of the transport coefficients. The surfaces are represented as dots, each dot is a transport state. Transitions from the blue dots into the green/red dots can be the usual transitions in the case of an inelastic inter-band scattering event (i.e. absorption/emission of optical phonons).
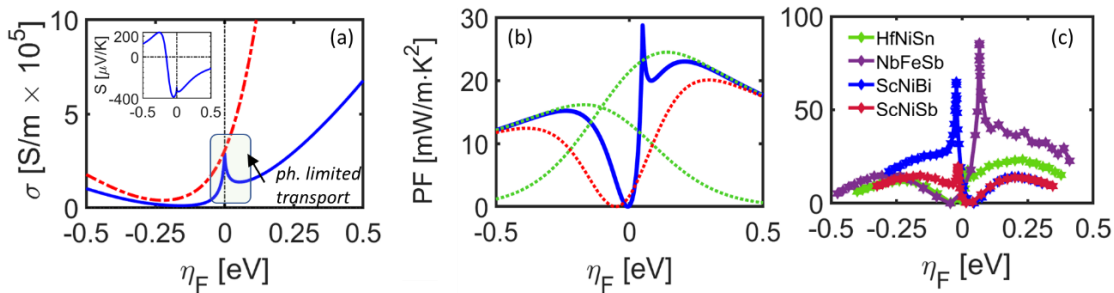
Figure 2: (a) electrical conductivity for very asymmetric conduction and valence bands in terms of effective masses (0.2 m_0 and 1m_0) and deformation potentials (3 eV and 6 eV) with a narrow bandgap of 0.4 eV at 900 K. The dash-dot red line is for the case when only scattering with phonon is considered (no with dopants). $\eta_F = 0$ represents the intrinsic Fermi level, the inset reports the Seebeck coefficient. (b) The peak in σ and the non-zero S in the intrinsic region, return an additional spike in the Power Factor (PF) which is a purely bipolar effect not captured by combining simple unipolar considerations, in dotted red lines and then combined in the green dotted line. (c) This effect is observed also in some narrow gap half-Heusler materials, reported in the legend, for $T = 900$ K.

First principles investigation of transport properties of 2D SnX$_2$ (X=S, Se) and Janus SnSSe monolayer

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Low-cost, earth-abundant, and environment-friendly materials have attracted the attention of the thermoelectric community.[1] Recently, there has been a surge in the study of 2D materials for their potential thermoelectric applications. Among the various studies, a recent report investigated the two-dimensional Janus monolayers WS-X (X=Se, Te) for high thermoelectric performance.[2] Breaking the structural symmetry plays a crucial role in tuning the electronic properties of 2D materials. Therefore, by converting a monolayer structure into a Janus monolayer the electronic properties can be manipulated. Tin-based chalcogenides show an interesting thermoelectric property and are earth-abundant.[3] SnX$_2$ (X=S, Se, and Te) has a layered structure with space group P$\overline{3}$m1. SnX$_2$ monolayers can be converted into a Janus monolayer by replacing the chalcogen atoms from the top or bottom layer with desired chalcogen atoms.

We have investigated the electronic and transport properties of the SnS$_2$, SnSe$_2$, and Janus SnSSe monolayer via density functional theory using Perdew-Burke-Ernzerhof exchange-correlation potential. The systems were modelled with a vacuum of 15 Å to minimise the interaction with periodic copies. Due to the presence of heavy Sn atoms, the effect of spin-orbit coupling (SOC) on the band structure was also investigated. All three monolayers exhibited an indirect bandgap and band degeneracy at the Γ-point. With the introduction of SOC, the splitting of the degenerate bands was observed. The dynamical stability was investigated by calculating the phonon dispersion curve. The transport coefficients such as the Seebeck coefficient, the electrical conductivity, the power factor, and the electronic thermal conductivity were evaluated using the BoltzTraP2 code based on the Boltzmann transport theory within constant relaxation time approximation. This study presents a systematic investigation of the electronic, transport properties of the three monolayers.
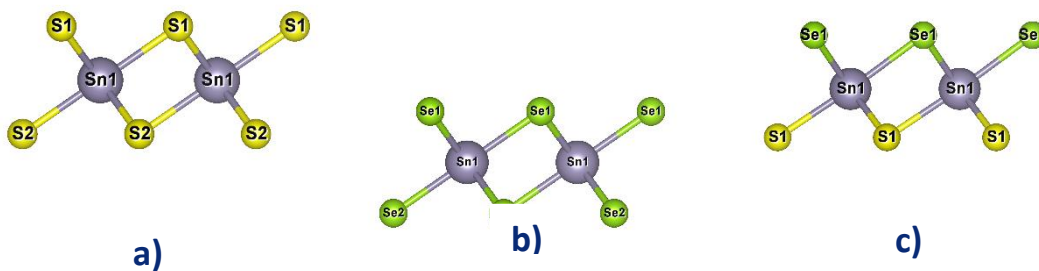
Schematic diagrams showing modelled monolayers a) SnS$_2$, b) SnSe$_2$,

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Topological Anderson Insulator in Cation-Disordered Cu2ZnSnS4

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Using *ab initio* calculations supported by experimental transport measurements, we present the first credible candidate for the realization of a disorder-induced Topological Anderson Insulator in a real material system. High energy reactive ball-milling produces a polymorph of Cu_2ZnSnS_4 (CZTS) with high cation disorder, which shows an inverted ordering of bands at the Brillouin zone center, in contrast to its ordered phase. Adiabatic continuity arguments establish that this disordered Cu_2ZnSnS_4 can be connected to the closely related $Cu_2ZnSnSe_4$ (CZTSe), previously predicted to be a 3D topological insulator. Band structure calculations with a slab geometry reveal the presence of robust surface states, while impedance spectroscopy coupled with resistivity measurements point to the surface-dominated transport which such states would imply; thus making a strong case in favor of a novel topological phase. Disordered CZTS along with the closely related CZTSe show significantly improved thermoelectric properties in low density, porous samples. This manifests as a reduction in thermal conductivity, enhanced by low-lying optical modes, without the corresponding loss in electrical conductivity, due to surface-dominated, scattering-resistant transport via the topological surface states. This potentially leads to a phonon-glass-electron-crystal type system, allowing for the exploitation of topological features via nanostructuring, to improve thermoelectric performance.
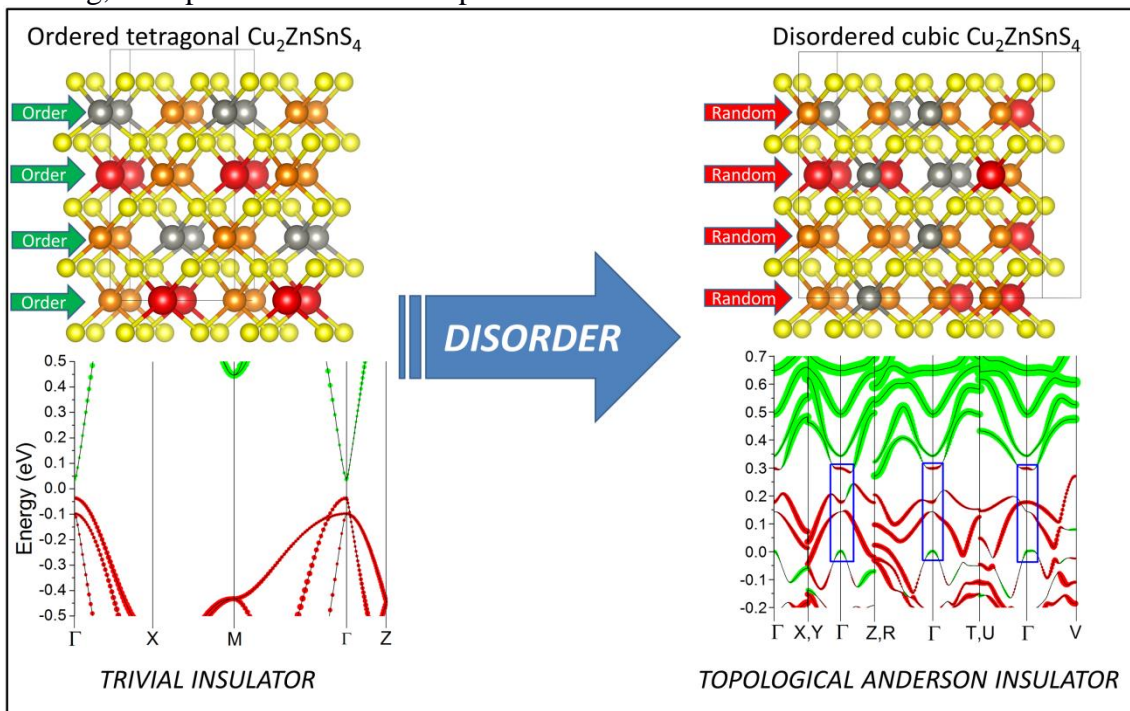
SESSIONE 5: Thermoelectric generators and devices (II)

Chair: Dario Narducci

Facile and low-cost fabrication of Cu/Zn/Sn-based ternary and quaternary chalcogenides thermoelectric generators

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In the present work, Cu/Zn/Sn-based ternary and quaternary chalcogenides inks were synthesized via hot injection and/or from ball-milled powders. The synthesized inks were used to fabricate thermoelectric generators (TEGs) based on _p_-type chalcogenide leg and _n_-type AZO leg via spin-coating and magnetron sputtering, respectively. Four different TEGs were fabricated using Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe), $Cu_{2.125}Zn_{0.875}SnS_3Se_4$ (CZTSSe), and Cu_2SnS_3 (CTS) chalcogenides. Thermoelectric transport analysis confirmed the respective _p_- and _n_-type natures of the chalcogenides and AZO. The absolute Seebeck coefficients of _p_ and _n_ components were compatible to be coupled in a _p-n_ device. Full-device performance analysis has been performed, and several factors affecting the performance of TEGs were investigated, including the composition, density, and presence of secondary phases in chalcogenide thin films. The maximum power obtained for CZTS, CZTSe, CZTSSe, and CTS TEGs at ΔT ~160 K were ~55 nW, ~240 nW, ~30 nW, and ~75 nW, respectively, making CZTSe/AZO TEG the best performing device.
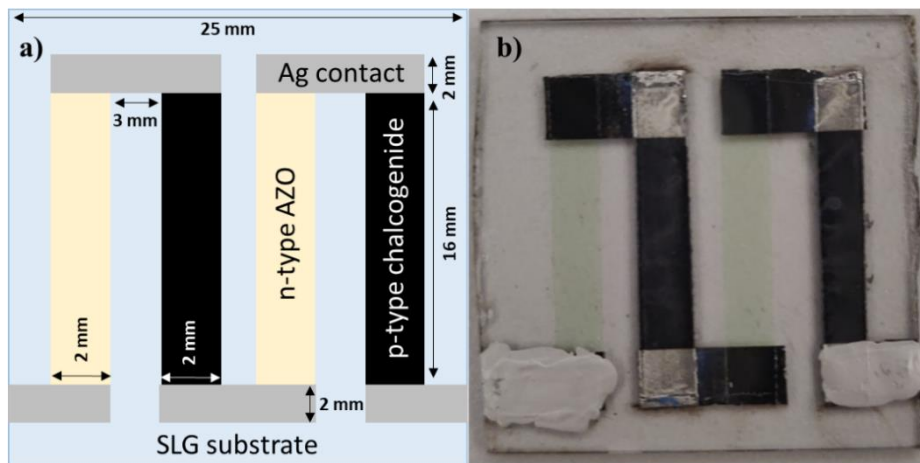
(a) Schematic design of a chalcogenide/AZO thin film TEG (not drawn to scale), **(b)** Fabricated thin film chalcogenide/AZO thin film TEG

Modelling and characterization of thermal transfer in a thermoelectric generator based on catalytic combustion

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The portable power needs are improving nowadays due to the large use of battery supplied devices. With this target a compact and lightweight thermoelectric generator (TEG) with the electrical output matching the common battery backup needs has been developed and characterized. The actual focus of the work is the study of the thermal transfer from the catalytic combustion to the thermoelectric modules used for the energy conversion. The target is to study how the hot side can drive the performances of the overall device through the management of heat flux and temperatures in order to achieve the maximum combustion efficiency and the compliance with the technological limits of chalcogenides materials. The study presents an experimental tests phase and a computational modelling phase, both leading to the definition of a new design for the hot side components. The design development has been enabled by the use of additive solution for the building of the new improved combustors. The new operating configuration to improve the performances at low mass flow rates has been thought. For the study of thermal coupling between combustor and modules, a local detailed analysis of combustor surfaces temperature profile using infrared images has been performed. Based on the data collected, a redesign of the hot side was carried out, with computational modelling of conductive and convective solutions of heat transfer enhancement. The resulting designs have been adapted to the technological limits of 3D building and produced for further developments.

Indice degli autori