

PROJECT FINAL REPORT



Next generation nano.engineered Thermoelectric Converters

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from concept to industrial validation

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4.1 Final publishable summary report

Executive Summary

Thermoelectric (TE) materials are semiconductor materials that can convert waste heat to electrical energy or utilizing electrical energy can cause a cooling/heating effect. The key material parameters, namely Seebeck coefficient, electrical conductivity, and thermal conductivity are all interdependent material properties. Due to this, designing a high performance TE material is not a straight-forward matter of material choice, but involves smart design of material interfaces.

In this project, the key strategy was to use nanotechnology to improve performance of promising TE materials in the bulk form. Selected materials were then further processed into modules, which were tested by key industry partners. While we failed to reach our target-power-output for the automotive application, important lessons have been learned. We have furthered our understanding of the fundamental sciences (physics, chemistry and materials sciences) behind nanostructured skutterudite, made important progress towards engineering useful modules and developed several new testing facilities. We assert that these results constitute a comprehensive step forward in the field of thermoelectrics.

The project initially narrowed the potential industrial applications of thermoelectric modules and the corresponding requirements for material development. The most attractive applications for the industry partners consisted of generating electricity from hot waste gases in car exhausts and industrial processes, with a maximum temperature of 600 °C. Due to the chosen temperature, skutterudites (SKT) were therefore the main focus of the material and module development in this project. In a second stage, the key material properties required for a stable operation of the device were identified: minimum figure of merit, allowable thermal expansion of the materials, choice, application and stability of electrodes, etc. On the cooling side, nanostructured bismuth telluride was the natural choice with a focus on the production of nanostructured materials rather than engineering of module, the later issue being largely solved.

Material fabrication was performed with extensive support from theoretical modeling. Skutterudites with various dopants, fillers, and other novel material concepts, such as ‘graded nanoporous’ TE materials, were investigated. During the project period, the most promising material for n- and p-type was chosen and fabricated in large scales to produce prototypes of the energy generation modules. Bismuth telluride-based materials were also developed and prepared in sufficient quantities to produce cooling modules.

We note that the production of efficient nanostructured material using the cutting edge processes used by the consortium (wet based chemistry, microwave, Spark Plasma sintering) proved to be more difficult and more time consuming than initially predicted. While many of these issues have been solved and prototype modules finally produced, we did not have sufficient time to solve some of the thermal and electrical connection issues which we discovered. A discussion of these issues is included in this report.

The project delivered three new different prototype modules: (1) a planar skutterudites modules for energy generation, (2) a novel skutterudites ring module design to minimize thermal expansion mismatch for automotive applications, and (3) a planar modules with nanostructured bismuth telluride for cooling applications. In parallel to these new modules, new facilities, simulation tools and test benches were also developed by the partners for testing the performance of materials or modules.

In addition, due to the largely unknown environmental and toxicological impact of nanomaterials, a comprehensive Life Cycle Assessment was done for skutterudites -based TE modules used for power generation in automobiles. The potential environmental impacts of these modules over their entire life were quantified. Hot spots were identified and the stage of synthesis of nanostructured materials appeared as the most impacting stage. These results showed potential benefits from energy generation during use stage and recycling at end-of-life. Besides the environmental assessment, the

toxicological risk of the materials along their life cycle was evaluated. Cytotoxicity studies suggested that skutterudites toxicity was similar to that of their metal components.

In summary, this project, “Next Generation Nano-engineered Thermoelectric Converters – from concept to industrial validation” has achieved the following objectives: (1) we have investigated in-depth and gained important new knowledge of the physics and chemistry of nanostructured skutterudite materials (2) we have developed and validated new material fabrication methods and (3) demonstrated that prototype modules can be produce for industrial testing. This has resulted in over forty journal and conference publications and the concepts were well accepted by the scientific community. In addition, we are among the pioneers in developing a prototype ring module for energy harvesting from the car exhaust gases, which has the potential for being further investigated by our industrial partners. Six patents have been filed, retaining the intellectual property rights within the consortium members for future exploitation to preserve the technological edge of the European Union.

Project Context and Objectives

The efficiency of any thermoelectric (TE) material is determined by the figure of merit-ZT, which is defined as $ZT = S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. Since S , σ , and κ are all interdependent material properties, increasing ZT is not a straightforward matter of material choice, but involves smart design of material interfaces. Fig. 1 shows a simplified schematic of a single TE couple for cooling or power generation. In the case of cooling, heat has to be pumped via electron (n-type TE) and hole (p-type TE) carriers from the cold to the warm end. In order to increase the performance efficiency of such a pumping, the thermal conductivity of both types of TE, which is responsible for the reverse heat conduction from the warm to cold end, should be reduced.

The field of TE advanced rapidly in the 1950s when the basic science of TE materials became well established. From 1960 to 1990, there has been only incremental gain in increasing ZT , but the TE industry grew slowly and steadily, by finding niche applications such as in satellites and space equipment, and medical applications, where reliability and predictability are very important. In Table 1 we list the best known TE materials where $(ZT)_m$

represents the highest reported ZT value. TAGS; the alloys $(\text{GeTe})_{1-x}(\text{AgSbTe})_x$ where $x \sim 0.2$, and Si-Ge alloys are widely used in TE generators for space applications, while Bi_2Te_3 is widely used for terrestrial cooling (particularly in commercial Peltier refrigeration devices with a ZT peak of 1.2 at room temperature for doped Bi_2Te_3). However, these applications were bedeviled by the low ZT of the materials. TE materials with higher ZT are important for the development of efficient energy conversion systems. For power generation, TE materials with $ZT \geq 2$ at around 800 °C are expected to be more efficient than solar energy devices. For lower temperature range between 300 to 500 °C, materials with $ZT \geq 2$ are expected to be very promising for recovery of energy from low level heat

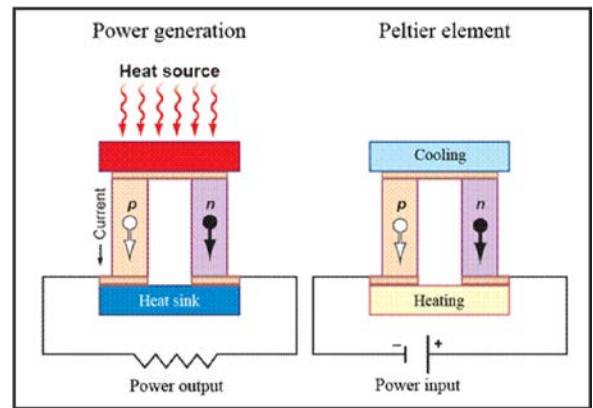


Figure 1. A typical TE module

Table 1. TE materials and highest ZT values and the T of best performance

Material	T_m (K)	$(ZT)_m$
Bi_2Te_3	300	1.2
TAGS	700	2.0
PbTe	650	1.0
Si-Ge	1100	1.0
Bi-Sb	150	0.7

source, e.g. automobile exhaust. For ambient temperature application, TE refrigeration will be competitive with compressor based conventional technology for TE materials with $ZT \geq 3$.

The past decade from 1990 has witnessed an increased interest for TE and significant research efforts; especially in USA and Japan. Attempts for improving TE material properties can be summarized into two different research approaches: one identifying new families of advanced bulk TE materials, and the other using low dimensional material systems.(1) For the advanced bulk material approach, host-guest crystal structures with rattling atoms, e.g. skutterudites, Clathrates and half-hausler materials, were introduced. (2,3) This is also called “phonon glass electron crystal” material. The skutterudites, such as $\text{CeFe}_3\text{CoSb}_{12}$, with Ce as ‘rattler’ atoms in atomic cages, are a family of compounds that has a potential for remarkable performance improvement since their thermal conductivity is relatively low. (2,4) Regarding the low-dimensional material approach, the introduction of NS constituents would introduce quantum-confinement effects to enhance the power factor, $S^2\sigma$. More importantly, NS materials with grain size in the nanometer regime have significant amount of grain boundaries. Grain boundaries are more selective for the diffraction of phonon as compared to that of electrons. This will result in a significant decrease of thermal conductivities and a relatively smaller decrease of electrical conductivity, which leads to an improvement of the ZT.

Advanced low-dimensional TE materials/architectures such as 1-D nanowires/nanotubes/nanorods has been theoretically predicted by Dresselhaus’ group to possess extremely high ZT values (5-10) compared to bulk state of-the-art ZT value of around 1. (5,6,7) Later, experimental explorations proved that 2-D super lattice structures ($\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ super lattice and $\text{PbTe}/\text{PbSnSeTe}$ quantum-dot super lattice) have the ZT of 2-2.5. (8,9) Their high ZT is due to the reduction of κ and enhancement of S. However, these advanced low-dimensional TE materials are not practical for large-scale commercial use because they are fabricated by atomic layer deposition processes such as molecular beam epitaxy, making them slow and expensive to fabricate and restricting the amount of material that can be produced. (10) There are also a lot of difficulties associated with TE module/device fabrication technology using these materials. Technology based purely on low-dimensional TEs, although offering a great potential for small-scale applications, is not readily transferrable to the industry. Therefore, there is still great/urgent need for high-performance TE materials based on bulk form, which can be easily transferred to industry.

In this project, the key strategy was to use Nanotechnology to improve ZT of promising TE materials in the bulk form. Therefore, this project will allow further steps of processing materials into module/devices which can be actually tested in industry. Based on the identified interesting applications and materials, the current module/device technology will also be developed during the project. Bulk nanostructured TE materials were the main focus of this project due to practical considerations of technological simplicity in making prototype modules in the later stages of this project. Bulk NS TE materials were fabricated using a bulk process rather than a nanofabrication process, which has the important advantage of producing large quantities and in a form that is compatible with commercially available devices (10).

Crystal doping/filling was also conducted to manipulate carrier concentration as well as rattling effect; therefore, S and/or σ could be enhanced and κ reduced. Theoretical studies gave suggestions and criteria for selection of new doping/filling materials.

TE nanocomposites are regarded as a new paradigm and the future of TEs (1). For NS materials, beside the presence of high density of defects, the composition of grain boundary also plays an important role in the overall properties and functionality. Thus engineering of the interfacial grain boundary offered further possibilities for the tuning of the overall materials

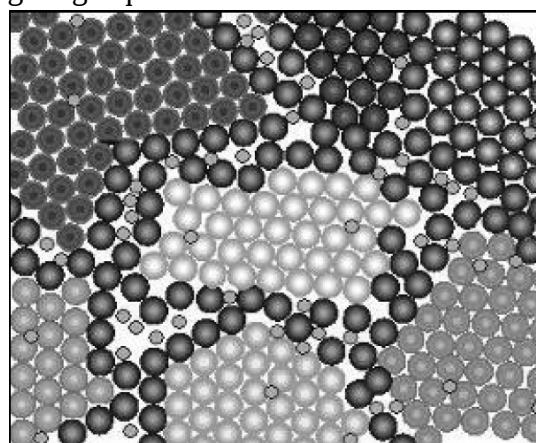


Figure 2. Engineered grain boundary in nanostructures bulk TEs

properties. Therefore, it was possible to develop NS TE composite materials with engineered grain boundary, consisting of one or more phases different from that of the nano-grains in the grain boundaries of TE phase; as schematically presented in Fig.2.

The main objectives of NEXTEC are categorized below:

1. Definition of system requirements

An important objective was to identify the most promising industrial applications of novel nano-structured TE and hence deduce the implications for the materials and modules to be developed during the project. This includes not just the TE properties of the novel nano-structured materials, but also other material issues relating to the design, fabrication and stability of the TE modules. Taking these into account was necessary to enable the industrial validation of the nano-structured TE materials.

2. Fabrication of novel nanostructured materials

After choosing the application scenarios, the next main objective was to fabricate novel and high-performance TE materials. We focused on development of state-of-the-art bismuth telluride system for cooling applications and the most promising SKT architecture for energy generation modules. Other novel material composition/architecture, such as nanoporous materials/metal foams were also investigated as potential TE material candidates. In this project, bulk NS TE nanocomposites were designed and developed by adding advanced low-dimensional TEs as well as immiscible ceramic oxides as additional phase to the matrix consisting of bulk NS TE materials. In this manner, the TE performance was further enhanced by the additional phases while the materials were easily processed for module/device fabrication due to their bulk-like nature. The additional phases also called “nano-inclusion”, had another function of hindering the grain growth during the high-temperature post fabrication processes such as reduction, compaction and sintering, and therefore preserved the excellent “nano-effects” of the materials. The in-depth investigation of the underlying physics was also undertaken with theoretical modeling validating our experimental findings.

3. Characterization and TE metrology development

Another important objective of NEXTEC was a reliable method for evaluation of the TE properties. Included in this, are the measurement of the Seebeck coefficient, the electrical conductivity, the thermal conductivity, the carrier concentration and the mobility of Bi₂Te₃- and CoSb₃- based nanostructured materials as a function of the chemical composition and microstructure from 20 to 1000 K. The measurements will be performed at each fabrication steps in order to chronologically correlate the change of the transport properties as a function of the microstructure. The measurement will be performed on spark plasma sintered, screen printed and electrodeposited materials. For this, we developed a round-robin process for transport property evaluation of the developed materials. In addition, development of novel metrology instruments that enable rapid and high-throughput measurement of electrical and thermal conductivities were also carried out in this project.

4. Module fabrication

One of the main objectives of NEXTEC was to incorporate the novel SKT materials into novel TE modules, to characterize the modules and to test their performance under realistic operating conditions. In order to achieve these objectives several sub-tasks had to be addressed, as follows. Conventional planar designs and a new ring configuration for a high-temperature TE module had to be developed and optimized. The TE powder had to be sintered into suitable form and the resulting pellets fabricated into modules. Another sub-task was to establish test benches to characterize the thermal and electrical performance of modules under ideal conditions, and to assess the reliability of these test benches, including a round robin. Additional test benches had to be developed in order to

assess the performance of prototype modules under realistic operating conditions. A further task was to establish system-level simulation tools, which used the measurement results to evaluate the feasibility of TE technology for the foreseen applications, e.g. generating electricity from hot car exhaust. An additional aim was to fabricate a planar module with improved Bi₂Te₃ and test its performance for cooling applications.

5. Life cycle impact analysis

The main objective of this work package is the evaluation of the environmental impact caused by the nanomaterials used in the fabrication of novel TE modules developed in this project. This task required, among other activities, designing a new framework for the life cycle impact assessments of nanomaterials based on the existing model ReCiPe 2008 (specifically, nanomaterials used for the fabrication of novel TE modules).

Main Results and Foreground

The major S&T tasks of NEXTEC were divided into five work packages that are listed below:

WP1: Definition of System Requirements

WP2: Theoretical Modelling and Simulation; Materials Selection and Fabrication

WP3: Physicochemical and TE Properties Validation

WP4: Module Specifications: Module Fabrication and Testing

WP5: Life Cycle Impact Assessment

Main results of each work packages are described below:

WP1: Definition of System Requirements

It was very important for NEXTEC to ensure that TE materials and modules were developed, which could potentially be used by the industrial partners. In WP1 the potential industrial applications of novel nano-structured TE were considered and the implications for material development and module design were derived. Most of the work was carried out by Siemens Electrolux, and SEAT, which are the industrial partners in the project.

The most promising application for SEAT involves generating electricity from the waste heat of automobile exhaust at 200–600 °C. The most attractive possibilities for Siemens also involved electricity generation, but with a much wider range of heat sources, for example diesel locomotives (exhaust gas at ~550°C), ship drives (exhaust gas at 300–600 °C) and single cycle power stations (flue gas at 450–600 °C). Note that automotive exhaust is by far the most challenging application, because the exhaust temperature and mass flow are highly variable depending on driving conditions, space is limited and weight is critical, whereas for most industrial applications the waste gas properties stay within a narrow range without occasional high-temperature peaks, thermal cycling is limited and space is plentiful. Nevertheless, there is an overlap in operating conditions for the applications so Siemens and SEAT defined a common application scenario, involving hot gas at 200–600 °C and liquid coolant at <100 °C. Furthermore the TE module should not contain any toxic materials and should be stable under cyclical operation.

These requirements rule out Bi₂Te₃ (too inefficient above 250°C), PbTe (toxic) and SiGe (far too expensive), and the consortium agreed that based on the partners' expertise skutterudites offered the most promise, with a target figure of merit $ZT > 0.8$ (averaged over the range of application temperatures).

In addition to the new TE material, Siemens identified additional material challenges for module development, which are critical for successful industrialization. The electrodes must not react with the TE legs, so a diffusion barrier may be necessary. The joining technology should be stable at module hot-side temperatures of at least 500 °C, but the joining process should not damage the skutterudites, which begin to degrade above ~600 °C. The inevitable thermal strains during operation should not break the module, so the thermal expansion coefficients of all materials should be compatible and the legs and joints need sufficient fracture resistance. Many module designs are possible, such as encapsulated planar modules, open planar modules and cylindrical modules, and the design should be chosen which limits thermal strain while optimizing conversion efficiency and offering good manufacturability. In operation a module must be connected to heat exchangers to both the hot gas and the coolant liquid. Since these are necessarily metallic the module electrodes must be electrically insulated while maintaining excellent thermal contact, which must be stable up to the highest operating temperatures and after thermal cycling. Finally, even the best module can only produce good performance if heat is effectively extracted from the hot gas and passed into the coolant, so the heat exchangers themselves must offer good thermal transfer for the given module geometry.

WP2 and WP3: Theoretical Modelling and Simulation; Materials Selection and Fabrication & Physicochemical and TE Properties Validation

Due to the extensive interaction between WP2 and WP3 the achievements for these two packages are presented together in this section.

Theoretical Modelling and Simulation

The main objective for the simulation group was to calculate the electronic structure and thermoelectric properties for nanostructured systems, in particular skutterudite systems. At the project start, no efficient scheme existed to calculate lattice thermal conductivity.

We have investigated the electronic structure of a range of TE materials of high technological interest, and also calculated thermoelectric properties from first principles. From simulations on Fe substituted skutterudite system, we find that about 30% in-mixture of Fe optimizes the power factor in the relevant temperature range. The effect can be for the most part explained through an electronic structure effect of the density of states, where the position of the Fermi level is altered due to fewer electrons in Fe compared to Co. Further, the lattice thermal conductivity has been calculated using the recently developed TDEP scheme. The results are in good agreement with experimental values. Our results clarify how an optimized power factor is achieved with 30% in-mixture of Fe in CoSb₃, and also demonstrate that all thermoelectric properties for these systems can be calculated reliably from first principles.

Materials Selection and Fabrication & Physicochemical and TE Properties Validation

Based on the identified materials in WP1 skutterudite materials have been chosen for power generation and chalcogenides for cooling applications. Several compositions of n- and p-type skutterudites have been fabricated by KTH, NCSRD and CSIC groups. Promising materials have been further scaled up and sent for module fabrication to SME partner CIDETE.

Synthesis of n- and p-type chalcogenides (Bi_{2-x}Sb_xTe_{3-y}Sb_y)

A variety of Bi_{2-x}Te_xSb₃ compositions were prepared using solution co-precipitation followed by thermochemical reduction, direct reduction in solution as well as mechanochemical alloying methods. Solution co-precipitation route includes the simultaneous precipitation of metal salts with the desired stoichiometry from an aqueous solution. The precursor is then exposed to thermochemical treatment of calcination under air and reduction under hydrogen to form the final TE phase. Reduction in solution route includes the simultaneous precipitation of metal salts with the desired stoichiometry from an aqueous solution, which is then exposed to a strong reducing agent that generates hydrogen and causes reduction of ions into their elemental form in the solution. In mechanochemical alloying route, high purity elemental powders were mixed according to the stoichiometric ratio and were then ball-milled using Zirconia lined milling jar and zirconia balls. Hexane was used as wet milling media/solvent and the reaction time for ball milling was set to 15 hours. In order to avoid any oxidation during milling, the jar was filled with argon gas. After milling the sample was heat treated at 350 °C for 3 hours under continuous flow of 5% H₂ to obtain the desired phase. Schematic of the process is presented in Fig 3.

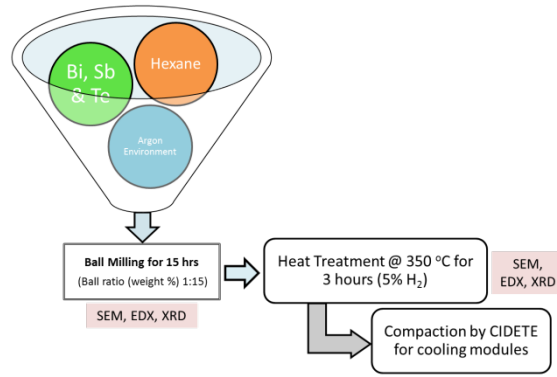


Figure 3. Mechanochemical synthesis of chalcogenide compounds.

Characterization of p-type $\text{Bi}_{0.4}\text{Te}_{1.6}\text{Te}_3$

SEM analysis was performed in order to investigate the morphology and the size of particles and grains. Particles after the ball milling and the heat treatment are in the range of few hundred nanometers to submicron, as shown in Figure .

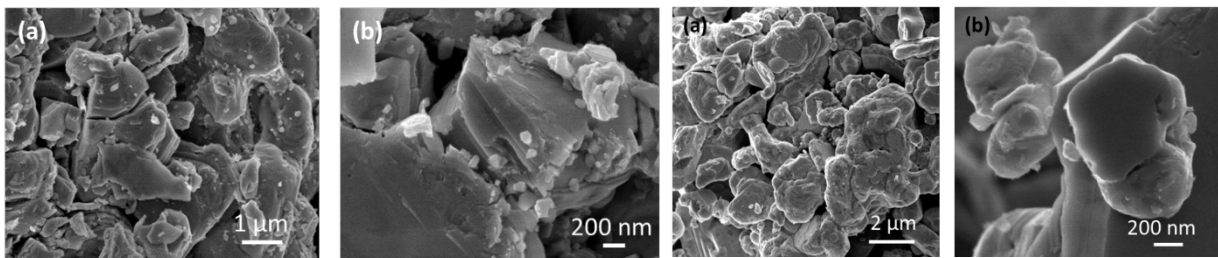


Figure 4. SEM from (a,b) ball milled, and (c,d) reduced sample

XRD patterns were obtained from only ball milled sample and heat treated sample. *XRD* pattern after the ball milling step, figure 6 (BLUE), which reveals that desired phase of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ is not formed completely at this stage. Heat treatment facilitated to achieve the final phase as shown in the second *XRD* pattern (RED). All peaks can be indexed with JCPDS Reference pattern # 72-1836 as shown in the inset of Fig. 5.

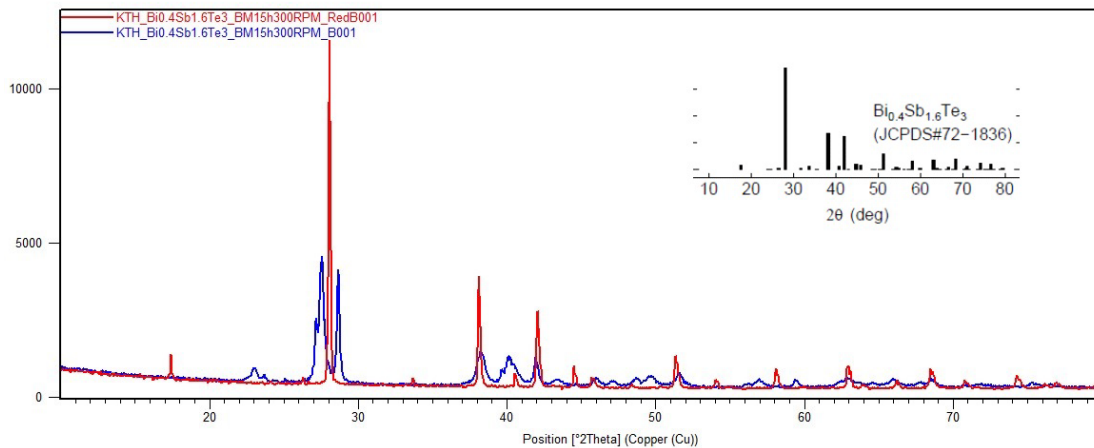


Figure 5. *XRD* patterns; ball milled sample (blue), ball milled and heat treated sample (red)

Transport data on NS Bi_2Te_3 sample is presented in Figure 6; results reveal a rather high ZT value of ca. 1.1 over a wide temperature range is achieved.

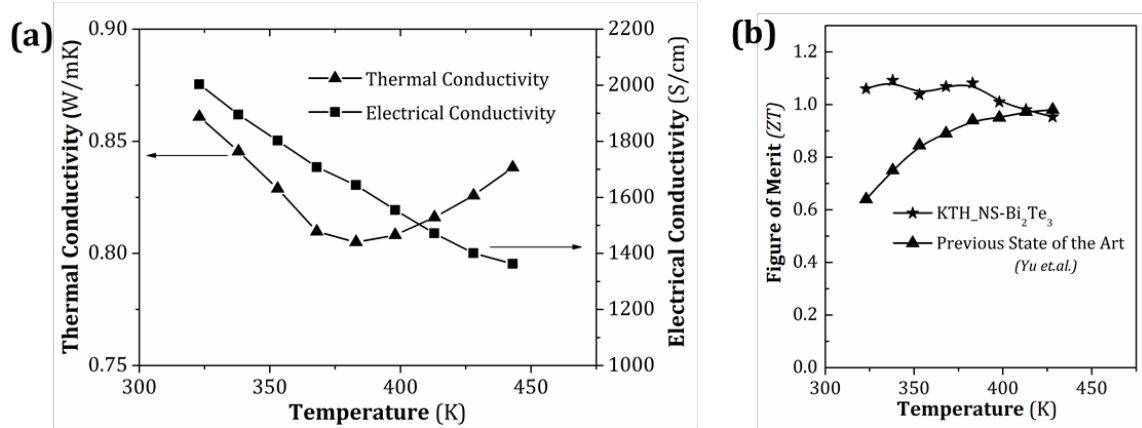


Figure 6. TE transport evaluations of Bi_2Te_3 ; (a) Electrical conductivity & Thermal conductivity, and (b) Figure of merit.

Synthesis of n- and p-type Skutterudites

The synthesis work on skutterudites continued to obtain materials with further improved TE performance. Several compositions with substitutional doping and crystal filling have been fabricated and evaluated.

KTH prepared skutterudite materials with the following compositions: (i) Fe/Te substituted CoSb_3 samples; (ii) Fe/Sn substituted CoSb_3 samples; (iii) $\text{M}_x\text{Fe}_y\text{Co}_4\text{Sb}_{12}$ (where M: Yb, Ce; $x=0.125$ and 0.250 ; $y=0.8, 1, 1.2$). The main skutterudite phase was fabricated using solution precursor method, which is also convenient for scale-up of selected compositions. Some nanopowders proved to be difficult to handle under industrial condition, therefore KTH performed some pre-agglomeration of these powders for a safer/easier handling at partner labs.

NCSR-D developed a microwave assisted fabrication method for graded TE materials, which is applied to skutterudite materials.

LEITAT developed new methods for the fabrication of large scale skutterudite nanopowders/nanofibers, namely: electrospinning and spray drying. All these processes require some form of thermal treatment to obtain the skutterudite phase. Compositions prepared include CoSb_3 , $\text{Ni}_{0.15}\text{Co}_{0.85}\text{Sb}_3$, $\text{Fe}_{0.2}\text{Co}_{0.8}\text{Sb}_3$, $\text{Ba}_{0.3}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$, $\text{Yb}_{0.02}\text{Ba}_{0.08}\text{La}_{0.05}\text{Co}_4\text{Sb}_{12}$.

KTH focused on p-type and n-type skutterudites according to the decisions taken during project progress meetings. The final set of p-type skutterudite was based on $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_{3-y}\text{Sn}_y$ and the n-type was based on $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_{3-y}\text{Te}_y$. The synthesis process was as same as before starting with metal chloride salts and a precipitating agent resulting in oxalate and oxides. After thermochemical treatments of calcination followed by reduction under hydrogen the final phase of materials have been obtained.

Table 2 shows the targeted composition as well as sample tags for the transport property evaluations.

Table 2. Produced skutterudite samples with their targeted chemical composition

Sample Tag	Targeted composition
KTH_SKUT_030_SPS01	$\text{Fe}_{0.1}\text{Co}_{0.9}\text{Sb}_{2.7}\text{Sn}_{0.3}$
KTH_SKUT_031_SPS01	$\text{Fe}_{0.1}\text{Co}_{0.9}\text{Sb}_{2.7}\text{Sn}_{0.3}$
KTH_SKUT_032_SPS01	$\text{Fe}_{0.05}\text{Co}_{0.95}\text{Sb}_{2.875}\text{Te}_{0.125}$
KTH_SKUT_033_SPS01	$\text{Fe}_{0.05}\text{Co}_{0.95}\text{Sb}_{2.95}\text{Te}_{0.05}$
KTH_SKUT_034_SPS01	$\text{Fe}_{0.05}\text{Co}_{0.95}\text{Sb}_{2.925}\text{Te}_{0.075}$

KTH_SKUT_035_SPS01	$\text{Fe}_{0.05}\text{Co}_{0.95}\text{Sb}_{2.925}\text{Te}_{0.075}$
KTH_SKUT_036_SPS01	$\text{Fe}_{0.1}\text{Co}_{0.9}\text{Sb}_{2.97}\text{Sn}_{0.03}$

The first two samples are compacted from the same batch of powders but with different compaction parameters. The KTH_SKUT_030_SPS01 is compacted at 475°C with 25MPa pressure and no holding time. On the other hand the KTH_SKUT_031_SPS01 was compacted at the same temperature but with 75MPa pressure and 3 minutes of holding time. We wanted to investigate the effect of compaction parameters on the samples.

Figure shows the XRD pattern of the compacted pellets performed on the polished surface.

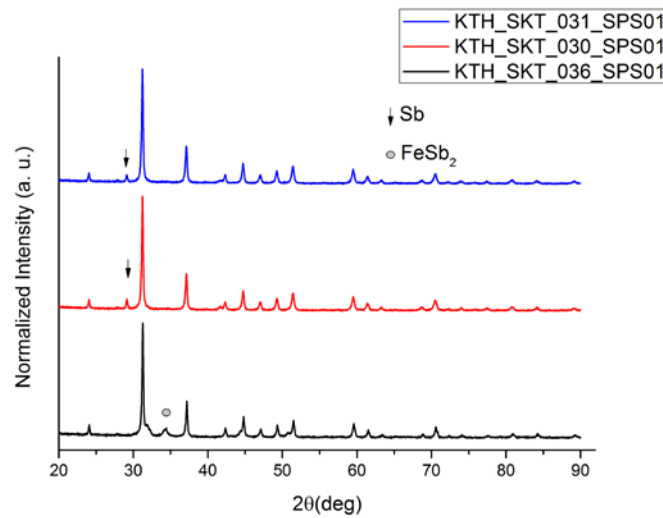


Figure 7. XRD pattern of last batch of synthesized p-type skutterudites

The data has the main phase matching ICDD Card No: 01-083-0055 for CoSb_3 . The compacted pellets show the major phase as skutterudite but the KTH_SKT_036 shows extra phase of FeSb_2 although the amount of tin (Sn) is lower than the other 2 samples. On the other hand the samples 30 and 31 show almost identical pattern as they are made from the same batch of powders. Therefore we didn't see that much difference here in the XRD pattern regarding the use of different compaction parameters.

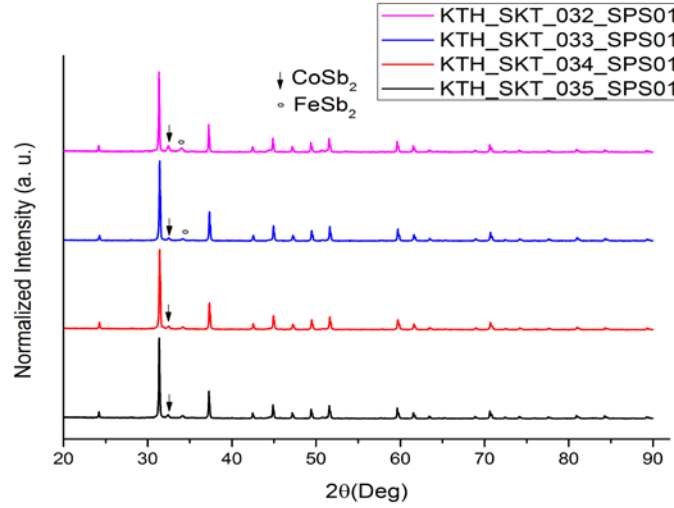


Figure 8. XRD pattern of last batch of synthesized n-type skutterudites

Figure shows the XRD results of n-type skutterudite samples. These patterns as well were matched with the same ICDD card and show major phase to be skutterudite. There are secondary phases of CoSb_2 and FeSb_2 but with increase in the amount of Tellurium they tend to disappear. These samples were sent to NPL for thermal conductivity measurement and further sent to CSIC for Power Factor measurements.

NPL performed the measurements on several of the samples and the Seebeck coefficient values as well as their thermal conductivity are summarized in Table 3 .

Table 3. Thermal conductivity and Seebeck coefficient values of the samples measured by NPL

Sample Tag	Seebeck Coefficient	Thermal conductivity
KTH_SKT_030_SPS1	81.36	3.70
KTH_SKT_031_SPS1	96.0	5.2
KTH_SKT_032_SPS1	58.9	5.6
KTH_SKT_033_SPS1	80.3	5.9
KTH_SKT_035_SPS1	81.30	6.06
KTH_SKT_036_SPS1	90.53	4.51

The samples show rather interesting room temperature Seebeck coefficients values for p-type skutterudite, therefore have been further sent to CSIC for PF measurements.

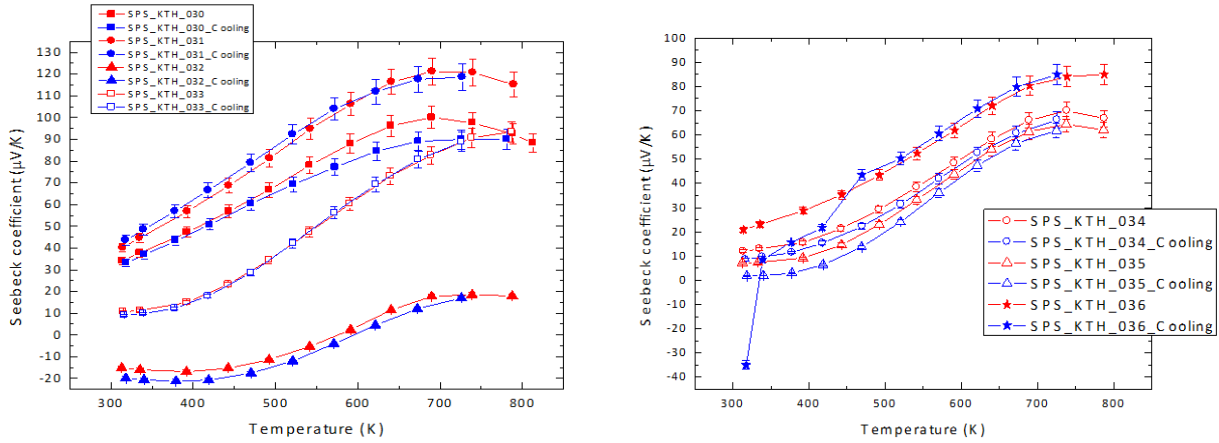


Figure 9. Seebeck coefficients of last batch of synthesized n- and p-type skutterudites

Seebeck coefficients of n- and p-type skutterudite samples have been measured in the heating and cooling ramp, in order to check the stability of the samples (Figure). Results did not show too much variation except for the sample KTH_036. The highest Seebeck coefficient of $+120 \mu\text{V/K}$ was obtained for the sample KTH_031.

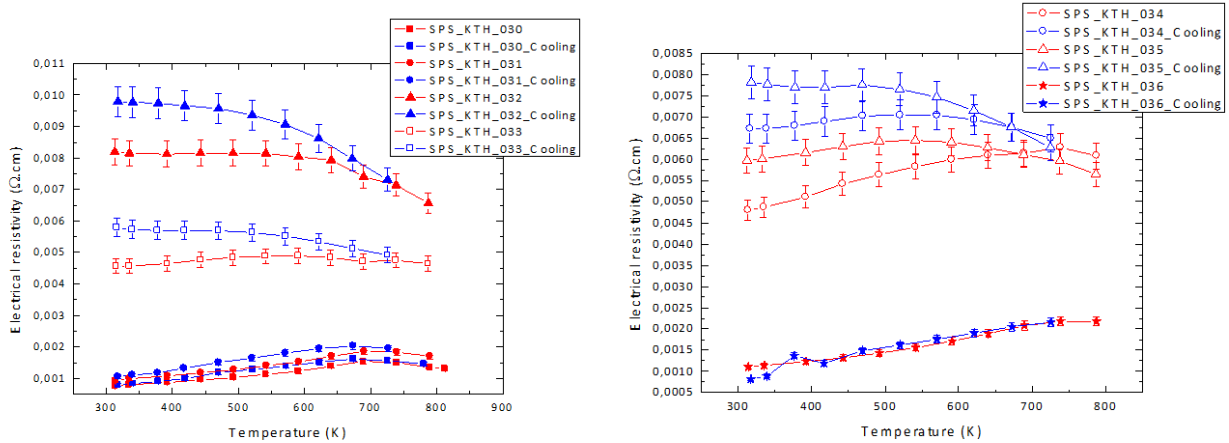


Figure 10. Resistivity of last batch of synthesized n- and p-type skutterudites

Resistivity of n- and p-type skutterudite samples have been measured in the heating and cooling ramp, in order to check the stability of the samples (Figure). Some powder was found in the chamber revealing that these samples decomposed during the measurements. Best results were obtained for the samples KTH_030, KTH_31 and KTH_036.

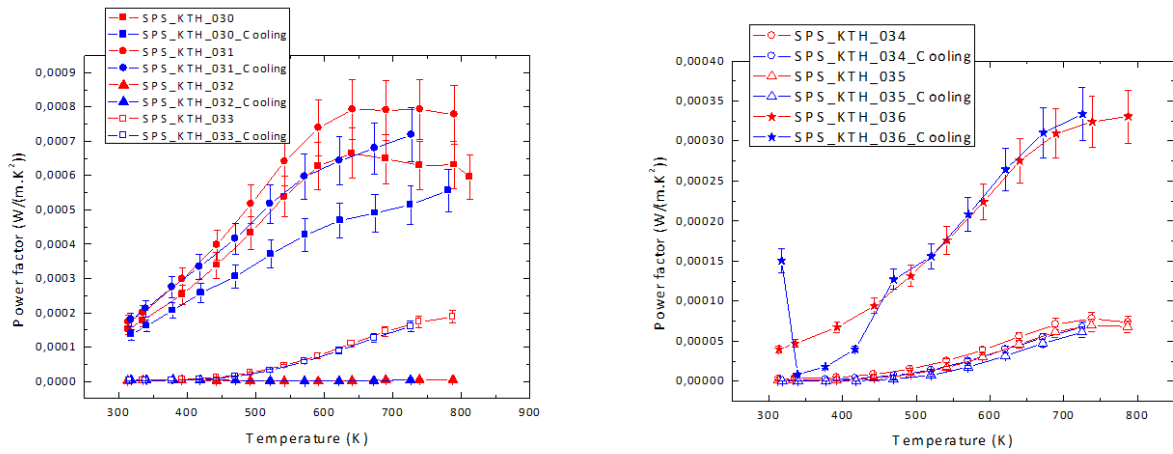


Figure 11. Power factor of synthesized n- and p-type skutterudites

Based on the CSIC measurements the power factor for n- and p-type skutterudite samples have been calculated and displayed in Figure . The highest power factor of $800 \mu\text{W}/(\text{m.K}^2)$ was obtained for the sample KTH_031.

The most promising p-type sample prepared by KTH displayed a ZT of 0.45 at 800K.

LEITAT studied the large scale production of nanostructured skutterudites by a precursor synthesis and using electrospinning or spray-drying techniques. In both cases, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Sb}(\text{CH}_3\text{COO})_3$ were used as precursors and they were mixed with the polymers polyacrylonitrile (PAN) or polyvinylpyrrolidone (PVP) in DMF solution. In case of electrospinning, skutterudite nanofibers were obtained using PAN (7,5wt%) as polymer, a ratio of Co:Sb (1:4,5) and a thermal treatment based on heating at $T=550^\circ\text{C}$ during $t=16\text{h}$ under argon. Images of the X-ray diffraction patterns as well as SEM photos are shown in **Figure 12**.

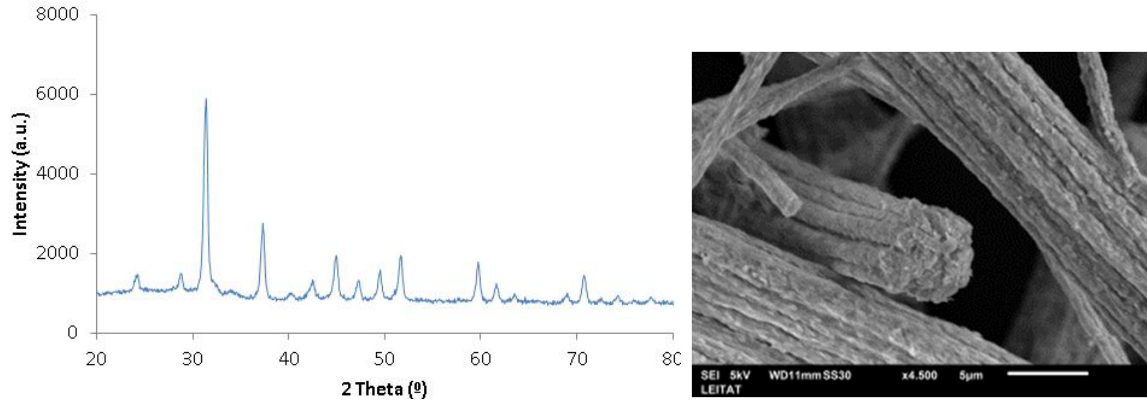


Figure 12: Images of the X-ray diffraction patterns and a SEM photo of the skutterudite nanofibers produced by electrospinning.

Spray drying of the precursor solution in DMF was performed using PVP as polymer. This polymer contributes to the reduction of the metal salts to CoSb_3 and, therefore, no reducing atmosphere during the thermal treatment was needed. Best results were obtained using a 8wt% PVP, a ratio of PVP:metals (1:1), a ratio of Co:Sb (1:3) and a thermal treatment based on heating at $T=550^\circ\text{C}$ during 6h under argon. SEM and XRD analysis (**Figure 13**) confirm the presence of microparticles and nanofibers of skutterudite. Quantities up to 50g of the precursor solid were obtained after spray drying and up to 20g of nanostructured CoSb_3 after the thermal treatment (40% yield). Moreover, doped and/or rattled samples of CoSb_3 ($\text{Ni}_{0.15}\text{Co}_{0.85}\text{Sb}_3$, $\text{Fe}_{0.2}\text{Co}_{0.8}\text{Sb}_3$, $\text{Ba}_{0.3}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$, $\text{Yb}_{0.02}\text{Ba}_{0.08}\text{La}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$) were produced using this method.

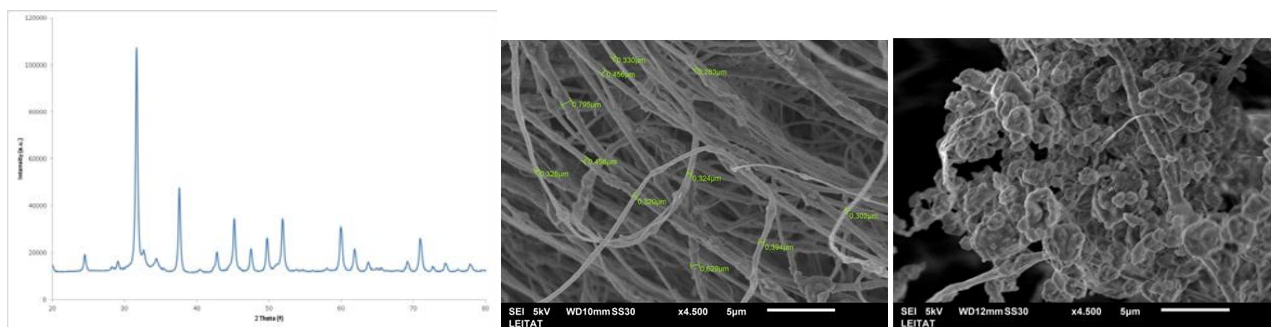


Figure 13: X-ray diffraction pattern and SEM images of the synthesized spray-dried and thermally treated CoSb_3 .

Although results were promising regarding nanostructuration and CoSb_3 production, no thermoelectrical characterization was possible due to the high carbon content (approx. 30 wt%) of the produced samples and, therefore, the difficulty to produce pellets for the Seebeck measurements. Future studies will be focused on the elimination of this carbon.

High performance n-type Skutterudites for ring TEG device

CSIC group got in charge of producing n-type skutterudite leg material. CSIC decided to use ball milling for nanosize particle production and spark plasma sintering for material densification, because it was needed to supply the industrial partner with large quantities of materials. Ball milling is an easy technique, scalable to the industry needs and is able to produce nano-grain size powder. The combination of this technique with spark plasma sintering produces nanostructured, compacted materials, which enhance the final TE properties of the material. Moreover, CSIC has also worked on the production of CoSb_3 by electrodeposition, to test the suitability of this technique for irregular, large surface covering.

In order to improve the TE properties of CSIC's bulk samples, and with the idea of introducing grain boundaries and defects in the material structure to reduce thermal conductivity, nanocomposites of CoSb_3 -oxides were proposed. Following this route, CSIC has been able to produce materials with thermal conductivities reduced down to $2 \text{ W.m}^{-1}\text{K}^{-1}$ through the control of the percolated nanocomposite formed during the process. The materials were characterized by different techniques such as XRD, SEM, EDS, Raman and TEM.

Figure 14 shows some of these images of undoped- CoSb_3 nanocomposite. This novel way to obtain percolated nanocomposite thermoelectrics has given very good results, and we are going to file a patent to protect the method.

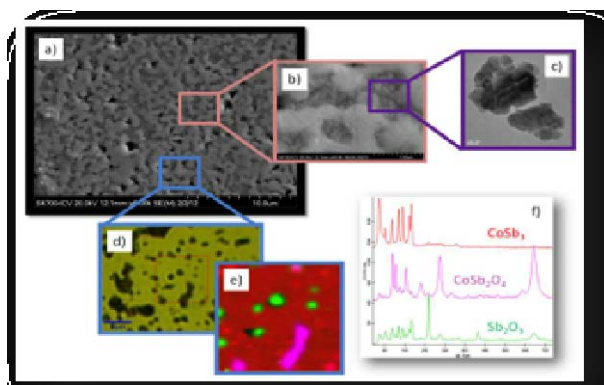


Figure 14. a,b) SEM images of a chemical attacked surface of a CoSb_3 sample; c) TEM image of the grain size; d) Optical image of the nanocomposite; e,f) Raman image and Raman shifts of the different phases.

The control of this process nanostructuring process and the understanding of the underlying process have allowed CSIC to obtain a material with a high ZT value of 1. In order to achieve that value CSIC group has doped the n-type material with Nickel, Tellurium, and both, obtaining the best results for Tellurium doping. Also the effect of filler was studied during the NEXTEC project, not showing any significant improvement on the final ZT value. The values of the ZT of all samples were obtained by measuring the power factor and the thermal conductivity at CSIC and IPM-Franhoufer.

Figure 15 shows the sequence of samples produced within the project by CSIC group

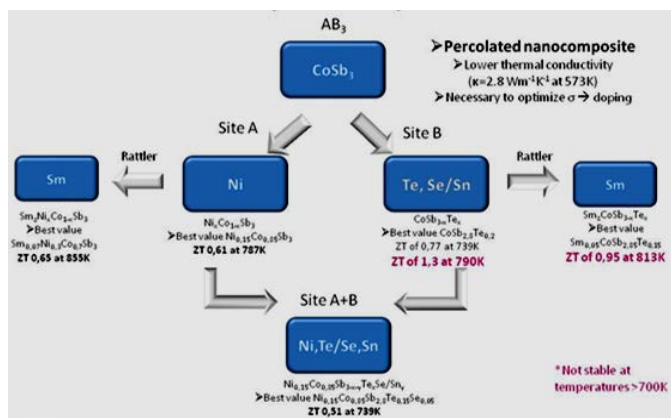


Figure 15. Sketch of the different samples produced at CSIC in order to optimize the ZT properties of the percolated nanocomposite.

Figure 16 shows a compilation of the different ZT values obtained within the project.

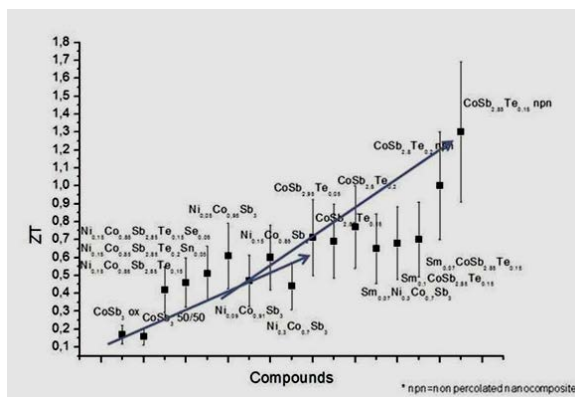


Figure 16. Best performing samples produced under NEXTEC project by CSIC.

Although a ZT over 1 was reached, those materials were not stable under the high working temperatures and finally, the $\text{CoSb}_{2.8}\text{Te}_{0.2}$ percolated nanocomposite was chosen for the ring device production.

A total amount of $\approx 1\text{kg}$ of n-type Skutterudite material has being produced for prototype fabrication at CIDETE during the whole project. Moreover, more than 150 CoSb_3 films were produced via electrodeposition form an organic solution in order to complete the task 2.5 of the work package 2. The CSIC group found the right condition to produce the stoichiometric phase after thermal annealing, and thick films of undoped- CoSb_3 were successfully obtained, as characterized by XRD and EDS. In order to get TE properties of the films a new lift-off process was also developed (Figure 17). And though this lift-off method was not easy to implement, finally some films were successfully detached for the sample and the first measurements of electrodeposited CoSb_3 films were performed in plane and cross-plane.

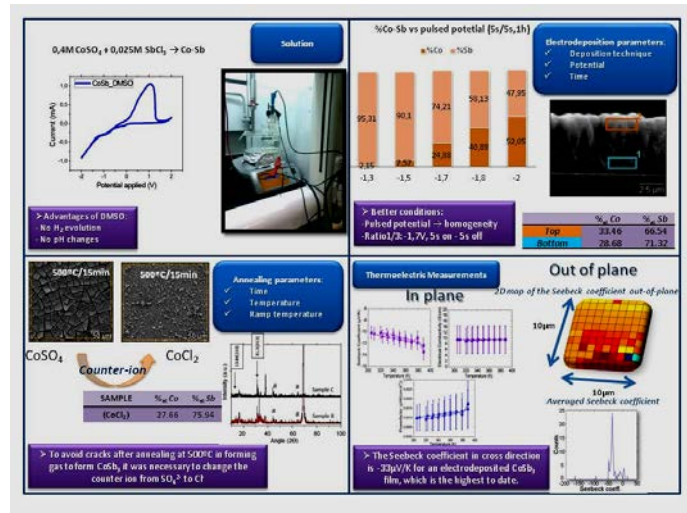


Figure 17. Brief summary of CoSb₃ thick films via electrodeposition

CSIC has also determined the conditions to obtain highly compacted p-type pellets from NCSR-Demokritos powders and to compact the powders produced by LEITAT. CSIC also performed measurements of the power factor of the pellets. This work will be part of a publication and a patent.

During the NEXTEC project, several round robin tests were performed in order to verify the TE measurements and other studies of this material were carried out, as for example, toxicity analysis.

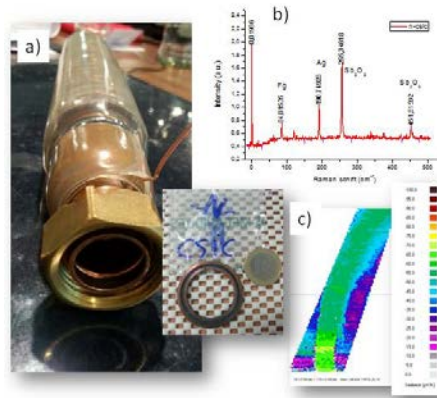


Figure 18. a) Ring prototype device and b,c) Raman spectra and the spatially resolved Seebeck coefficient of one n-type ring measured by PSM.

Extension of NPL capability to measure thermoelectric transport properties

NPL has participated to the general WP3 effort to characterise materials properties by measuring Seebeck coefficient, thermal conductivity and electrical resistivity for a range of samples. Beside this general “measurement service”, a number of facilities have been developed or investigated to answer some important questions related to nanostructured TE materials or specifically Skutterudite for high temperature applications. NPL extended their capability to measure thermal conductivity to small pellets about 1.5 cm in diameter and down to a few mm in thickness. A few examples of thermal conductivity measurements and comparison with reference samples is given in Table 4 and Table 5 :

Table 4. Thermal conductivity of different samples produced during the NEXTEC project measured at various temperatures.

Round Robin Skutterudite Samples	Thermal Conductivity κ (W/m.K)				Average κ_{ave} (W/m.K)
	At 30 °C	At 45 °C	At 60 °C	At 75 °C	
KTH_SKT_005_SPS01 (AEPK)	2.06	2.46	2.18	N/A	2.23
KTH_SKT_006_SPS01 (AEPJ)	2.50	2.31	2.38	N/A	2.40
CSIC-SPS-775 (AEPR)	1.55	1.47	1.45	1.61	1.52
CSIC-SPS-821 Demokritos (AEPT)	2.14	2.28	2.29	2.03	2.19
CSIC-SPS-809 Demokritos (AEPZ)	2.16	2.21	2.17	2.20	2.19
CSIC-SPS-775 Demokritos (AEQA)	2.78	2.87	3.11	3.05	2.95

Table 5. Thermal conductivity measurements for some reference samples and comparison with the accepted value.

Reference Material Sample	Thermal Conductivity κ (W/m.K)			Measured κ_{ave} (W/m.K)	Accepted κ_{ave} (W/m.K)
	At 30 °C	At 45 °C	At 60 °C		
Pyroceram (BCR-724)	2.59	2.55	2.61	2.57	3.89 [3]
Perspex (NPL 05/01)	0.78	0.49	0.66	0.64	0.19 [4]
Puren foam (NE-B2 40 HT)	0.04	0.03	0.05	0.04	0.023-0.026 [5]

Measurement of pellets uniformity and isotropy.

The measurement of the anisotropy of the transport properties of TE materials is a very important factor for the design of TEG systems. The transport properties of some of the best TE materials, such as Bi_2Te_3 , are anisotropic. Skutterudite is expected to be isotropic, however, due to the uniaxial pressure exerted on the powder during sintering, some degree of anisotropy might arise in the material.

Two measurement methods have been developed from scratch to measure the anisotropy of the Seebeck coefficient (at NPL) and of the electrical conductivity at room Temperature (3D-VdP at Fh-IPM, see next section) during the NEXTEC project.

In order to make a mapping of the Seebeck coefficient anisotropy, discs of TE material have been cut into cubes (Figure 19)

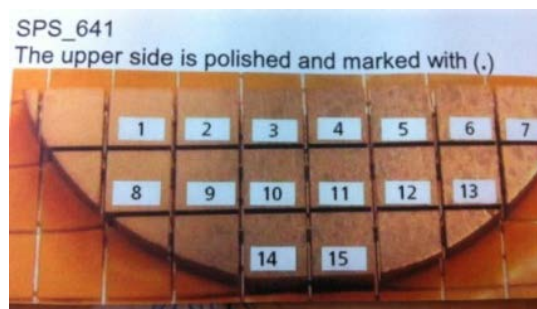


Figure 19. Disc-shaped compacted CoSb_3 -Skutterudite (CSIC-SPS 641) cut in 15 cubes. The size of the cubes is for this example $2 \times 2 \times 2 \text{ mm}^3$.

Each cube was measured with each of the six faces oriented alternatively upwards. The reported relative uncertainty (5.8%) was calculated according to the “Guide to the Expression of Uncertainty in Measurement (GUM)” and is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95%. The results obtained for different samples are shown in Figure 20.

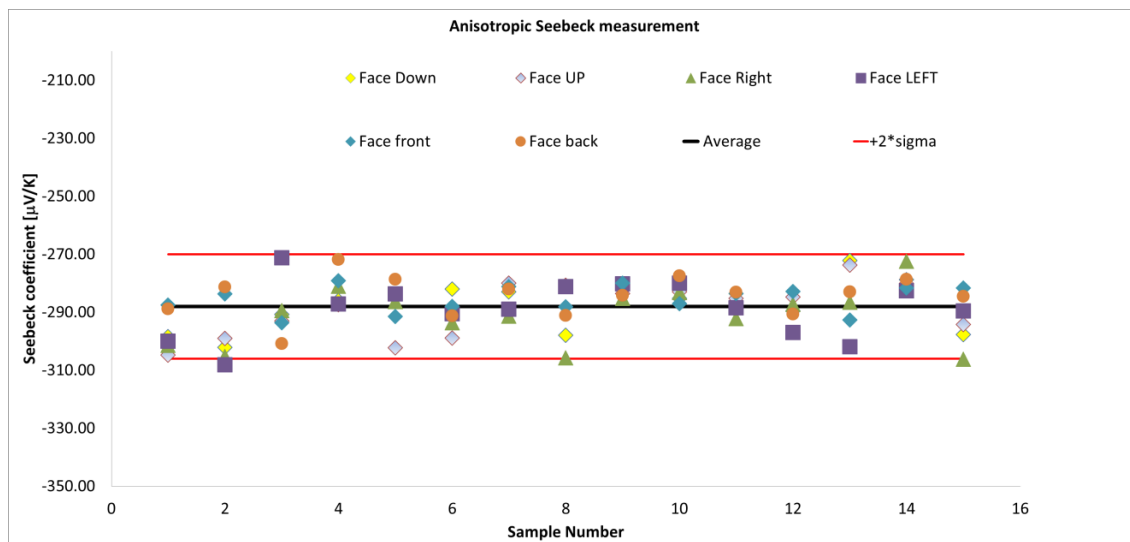


Figure 20. “Anisotropic Seebeck measurement” and processing uniformity.

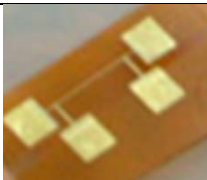
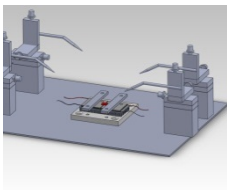
According to our results, no systematic Seebeck variation can be found in samples processed using Spark Plasma Sintering (Figure 7).

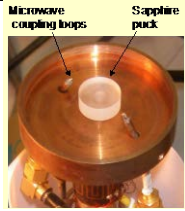
Measurement of thin-films.

Part of the initial focus of the project was on new methods to produce thin TE films. Accurate characterisation of TE properties of thin-films is notoriously difficult; this due to either the presence of a substrate or the heat dissipated in the environment by the detached films.

NPL has investigated a number of methods to measure transport properties for thin-films. These techniques and some relevant characteristics are summarized in Table 6.

Table 6. Techniques investigated for the measurement of transport properties of thin films at NPL:

Thermal conductivity measurement based on thermal and electrical transfer function such as the 1, 2 or 3-ω methods. We found that this methods are generally accurate and can be used directly on conducting samples if the heating circuit is patterned on a Kapton film; however their reliability is more doubtful for films thinner than 100 nm	 Heating circuits patterned on Kapton film
An “air-bridge” set-up to measure in-plane Seebeck coefficient and van der Pauw resistivity. Measurement of in-plane Seebeck is accomplished by bridging the sample across the two temperature controlled stages. Micro-thermocouples held in place by micromanipulator or test socket are used to measure surface temperature and	

potential. A relative uncertainty of 12.3 % has been calculated in air for temperatures up to 370K	Schematic of bridge system to measure TE thin film in-plane properties
For ultra-thin film, which maybe damaged during electrode deposition, a microwave dielectric cavity method can be used to measure sheet resistance. If the dielectric loading element has a strong temperature dependent permittivity (for example SrTiO_3) the method can in principle be extended to measure both thermal conductivity and heat capacity.	 Microwave cavity with sapphire puck and microwave coupling loops.

Nanoscale measurements

NPL has also used scanning probe microscopy to evaluate the lateral variation of the different transport properties at the nanoscale (Figure 2). Three new techniques were implemented to measure, electrical resistance, thermal conductance and thermopower.

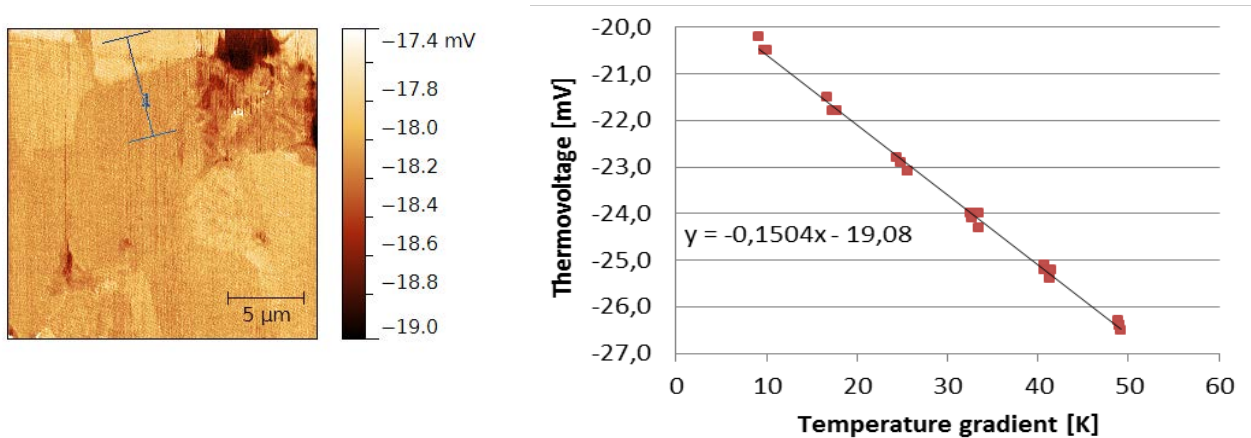


Figure 21. Scan of NIST Bi_2Te_3 reference sample with newly developed thermopower AFM technique at NPL. Line indicates position of the section

A key outcome was that, while conductance measurements are usually reliable, conductivity measurement depends critically on (1) the exact value of the contact area between the tip and the surface and (2) on the transport model (classical or ballistic) used. Unfortunately, AFM is right in the range where both mechanisms will contribute, depending on the exact value of the mean-free path value for the phonons or the electrons. Therefore, a reliable value for thermal or electrical conductivity cannot therefore be trusted yet from these measurements.

Module performance measurement: NPL has also developed a capability to measure the performance curve of module up to 950K (Figure 22). An inter-comparison between NEXTEC partners has been conducted.

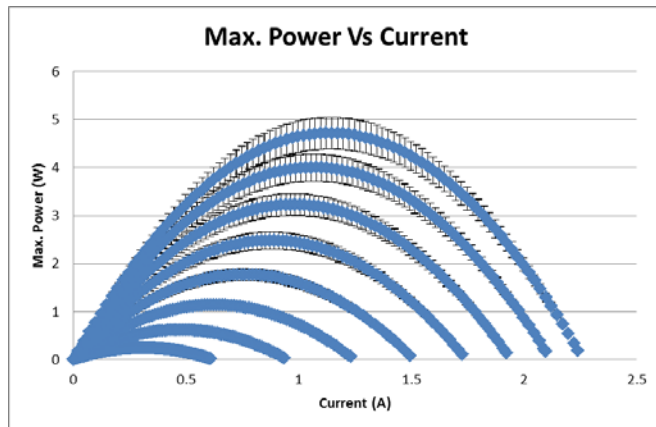


Figure 22. Power measurements of some modules produced on the NEXTEC project.

Extension of Fh-IPM capabilities to measure thermoelectric transport properties

3D-VdP method

There was a need in TE materials research to quickly measure the electrical conductivity of a sample in various directions in the case of materials with anisotropic crystal structure like bismuth telluride, most oxides and some silicides. In addition, anisotropic material properties can occur in sintered samples due to the linear force during sintering. Prior to the project start the most usual method was to cut bars from samples thicker than 1 cm. This method is difficult to implement especially when the samples are sintered, and the method is not free from artifacts. Difficulties arise because sintering tools are usually made of graphite and they break easily when the sample is too thick. The methodology is also flawed because the degree of anisotropy of a sintered material is a function of the sample thickness. The solution found in NEXTEC was to rework the data analysis used along with the Van der Pauw method in order to be able to extract the tensor electrical conductivity of samples with unusual aspect ratio (cube). The method has been tested for cube down to 2 mm. It has been shown that some anisotropy can be found even for Skutterudite material, which is an isotrope material, which to some extent reflects the uniaxial nature of the sintering process. A joint publication has been made with KTH and CSIC.

VdP-SRX

Common power factor measurement systems like the ZEM from ULVAC make use of bars for the electrical properties measurement. In addition, disc or square shaped samples for the thermal conductivity measurement are necessary. This additional sample preparation slowed down the speed for material screening in NEXTEC. Therefore a measurement system was developed at IPM in order to be able to measure the electrical properties on the same sample used to measure the thermal conductivity. The system has been tested extensively during the project, providing valuable measurement results to project partners. It has been found that the electrical conductivity could be measured accurately with our system. The origin of the measurement bias, if any at all, has been found to be material instability. Structural change (cracks, bubbling, strong oxidation) are likely to decrease the thermal conductivity but depending on the geometry and orientation of this structural change this can lead to an apparent increase of the electrical conductivity. This apparent increase of the electrical conductivity takes place when there is decoupling between the voltage probe and the sample (oxidation) and through inhomogeneity (crack, bubble) in the bulk. A joint publication has been made with KTH.

ZT-Meter for bulk samples

The simultaneous measurement in the same direction of the transport properties of TE materials is highly desirable for all the above mentioned reasons. This is an objective that is pursued at Fh IPM since 2006, who does have a working prototype since 2008. Originally, the measurement system was developed for disk (diameter 10 mm) having a thickness of 5 mm and has been tested rather successfully with bismuth telluride and lead telluride based materials. It has been shown now that cubes ($5 \times 5 \times 5 \text{ mm}^3$) of Skutterudite are measurable as well, i.e. anisotropy has been also measured on this material at high temperature (up to 820K). Measurement results have been cross-checked with the measurement technics available by the consortium. It has been shown that this measurement system is very suitable for materials screening. It must be underlined however that the simultaneous measurement in the same direction of the transport properties of TE materials is very challenging because the sample geometry cannot be optimized for each particular transport property. NEXTEC has shown with the 3D-VdP method that there may be solutions that could also be adapted to the IPM ZT-Meter within future projects. ZT-meter is commercially offered and has been advertised at the European Thermoelectric Conferences.

ZT-Chip for thermoelectric films

When it comes to large surface and low cost TE devices, the contribution of TE films may be significant. The success obtained in other areas with printed electronics is an encouragement to try to print TE devices. One challenge that has been addressed successfully in the project is the chip-based TE characterization of printed TE material at Fh-IPM. The thermal conductivity is measured using the “on-top” 3Omega method (presented at the European Thermoelectric Conference, Noordwijk). There are test structures on the chip to measure the Seebeck coefficient and electrical properties using the VdP and 2Omega method. These properties could have been measured, if the films were electrically conducting. The measurement technics is very suitable since the material could be printed on a dedicated area of the chip accurately at LEITAT.

Stamp ZT-Meter

Many samples have been produced in Nextec during 3 years. Almost all the samples have been measured at high temperatures, causing huge preparation efforts. A fast screening method might have removed the low performing samples from the measurement list at an early stage. This screening is efficient only if electrical and thermal properties are measured without the time consuming preparation. Since no commercial measurement system was available to fulfill these requirements, Fh IPM modified the ZT-chip for the use as a stamp on polished bulk surfaces. Here, first results are planned to be presented at the European thermoelectric Conference 2014 in Madrid. In this technique we use test structures that are microstructured on a flexible foil. These foils can be shipped to customers together with the measurement system that enables simultaneous 3Omega, 2Omega and VdP measurements; no costly sample preparation is needed (except surface polishing to minimize the thermal contact resistance). Besides this polishing step, the measurement is non-destructive, as the foil only has to be pressed on the surface of the sample for measurement.

Conclusions and outlook

We have investigated the electronic structure of a range of TE materials of high technological interest, and also calculated thermoelectric properties from first principles. Several new materials composition for skutterudites, where substitutional doping and filling the crystal lattice, as well as graded material concept and nanocomposite formation strategies have been applied. TE thin films were also developed and proved to be unstable for testing. Several novel methods have been developed for the fabrication of the TE materials. ZT values of up to 1.5 have been achieved within the consortium on n-type, and 0.45 for p-type skutterudite materials. Scale-up of fabrication of some selected compositions have been successfully implemented and large quantity powders were delivered to partners for module fabrication.

Two measurement methods have been developed from scratch to measure the anisotropy of the Seebeck coefficient and the electrical conductivity at room Temperature. The project developed TE measurement methods with sufficient accuracy to differentiate between materials with different compositions and structure and to provide support in the measurement of power harvested from systems in realistic thermal conditions.

WP4: Module Specifications: Module Fabrication and Testing

The main focus within the NEXTEC-project was to develop novel nano-structured TE materials and integrate them into high-temperature modules for electricity generation from waste heat, for example from car exhaust or industrial plants and large motors. Within WP4, the focus was given to the validation of the optimized materials, which were chosen, analyzed and sintered in WP1 to WP3. One of the biggest challenges is the fulfilling of all requirements, once the materials were integrated in modular units.

For testing under realistic conditions, several test-benches had to be built up and simulations had to be carried out. Since the approach was to achieve a stable working system also within high temperatures (up to 550°C) and real working conditions, the problem of thermal stress in planar modules leave us to evaluate additionally a novel ring configuration. The expectation was, that thermal stress would be working in favor of the whole module performance within this configuration.

A comparison of planar and ring-module configuration was carried out.

Design of the Test benches

- *Test bench for conversion efficiency at Siemens*

To coincide with the start of the project Siemens purchased a test bench from TEC COM GmbH (Fig. 23), with which planar TE modules can be characterized under controlled conditions (up to 550°C in air or N₂). Data sheets for commercial modules can thus be independently verified, and the results used for optimizing the design of TE generator systems for industrial applications.

The test bench (MTEC: Measurement of Thermal-to-Electric Conversion) has a cartridge heater at the top, then a reference block of ST37 steel below which the planar TE module is placed. Underneath is another reference block, a second cartridge heater and finally a water-cooled plate. This assembly is pressed together with an adjustable force. Thermocouples measure the temperatures at known locations within the reference blocks, so the heat flux through the module can be calculated using the known thermal conductivity of ST37. Once a stable temperature difference has been established across the module its current-voltage characteristic is measured using an electrical load. Within the project Siemens developed and optimized measurement protocols and wrote software (Matlab) to automatically analyze measurement data, e.g. by interpolating it and generating appropriate graphs.

Siemens also has a test bench to thermally cycle power generation modules, keeping the cold side at ~80°C and heating the hot side up to ~450°C. This can be used in conjunction with the MTEC to investigate the long-term thermal stability of TE modules.

- *Application-oriented test bench at Siemens*

To ensure the industrial relevance of novel TE modules Siemens requires a test bench whose design is close to the application scenario for generating electricity from waste heat. Siemens therefore designed, built and optimized an application-oriented test bench, whose final version is shown in Fig. 24. An adjustable blower blows air (up to 85 g/s) through an electrical heater (up to 3.3 kW) into a TE generator (TEG), where it passes over a fin-type heat exchanger, which delivers heat to two pairs of TE modules. Heat is removed from the modules by cold plate heat exchangers, which use flowing water (in counterflow to the hot gas stream). The modules and coolant plates are clamped into position against the gas heat exchanger using steel plates held by adjustable pressure springs. The air leaving the TEG is still hot so for lab safety reasons it is passed through an air cooler.



Figure 23. MTEC test-bench for module conversion efficiency available at Siemens. (Source: Siemens)

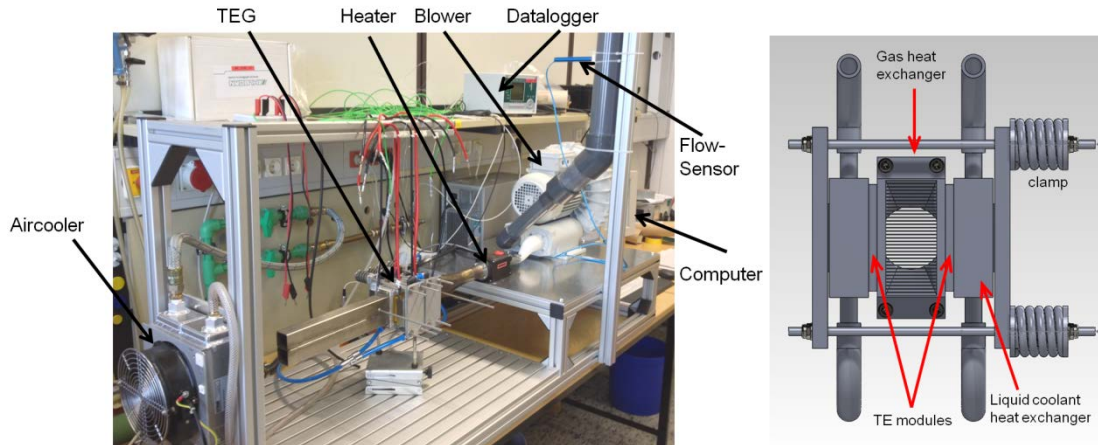


Figure 24. Application-oriented test bench for TE modules developed by Siemens. (a) Overall view. (b) Schematic end-on view of modules sandwiched between heat exchangers. (Source: Siemens)

The test bench measures the temperatures of the hot and cold sides of all four modules, as well as of the hot air and cooling water both entering and leaving the TEG. Furthermore the flow rates of both air and coolant and the gas pressure drop across the heat exchanger are measured. The current–voltage characteristics of all four modules are determined with the help of an adjustable electrical load ($0.05\text{--}3.34\ \Omega$), which Siemens custom-built to cope with the low voltages and high currents of TE modules. All measurement parameters are continuously logged by computer. Siemens built interfaces between the computer and the blower, heater and electrical load, and wrote control software for the entire test bench to carry out fully-automated measurements.

- *Test benches for in-situ measurement of rings at CIDETE*

CIDETE has built a test bench for the in-situ measurement of the manufactured rings (Fig.25). The set-up consists on a cooling system based on commercial TE modules and a hot resistance. It allows cooling the outside part of the measured ring while heating in the inner part. For the proper performance of the test bench and in order to reduce thermal losses, thermal grease was also used. The maximum hot temperature reached was $300\ ^\circ\text{C}$ and the gradient of temperature achieved on each measurement was $200\ ^\circ\text{C}$.

We want to emphasize the special importance of this primary set-up. It allowed us measure the as-pressed rings of the different NEXTEC materials, and to find the best pressing conditions for the best TE performance. Several measures of the different pressed rings have been done using this test bench in order to select the materials in the final generation TE modules.

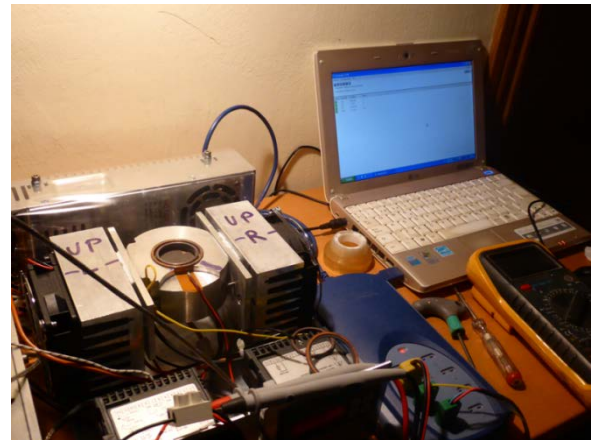


Figure 25. Testing bench for in situ single ring performance

- *Test bench for thermo generator application at SEAT*

STC has developed a test bench in order to measure not only the power of the rings demonstrator in real life conditions, but to measure the temperature distribution across the entire system, in order to know where the heat flow has its bottleneck (Fig. 26). This can help to find other options to have the maximum temperature difference in both sides of the material, as important as the own material characteristics regarding the whole TEG efficiency.

The demonstrator has been instrumented with thermocouples to read pipe surface temperatures and inner and outer ring temperatures at the beginning, mid and end zones. Gas and water intake and exhaust temperatures are also measured.

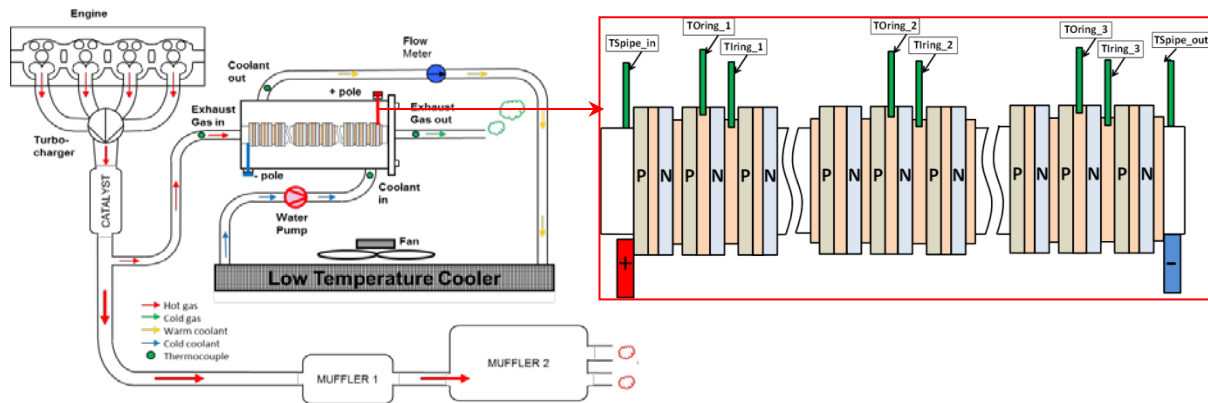


Figure 26. Test bench developed by SEAT

A preliminary test with a heater and a blower has shown that the first ring TEG does not give any electrical power. However, the temperature distribution and heat flow through the TEG can be measured.

The TEG test bench uses car components in order to have a near car behavior. The water pump, radiator and fan are the same than in the target car (Ibiza 1.2 TSI). The exhaust gas comes from the exhaust of one of SEAT engines on STC engine test bench facility, as shown in Fig. 27.

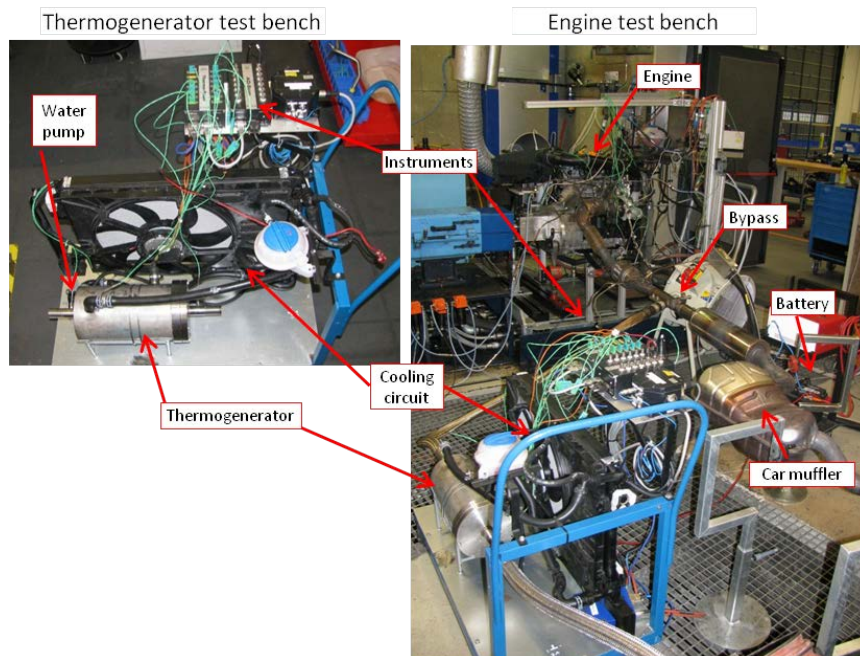


Figure 27. Test bench with conditions of target car, Ibiza 1.2 TSI.

Module Design

• Ring Configuration

The first step for the ring configuration module manufacture was the skutterudite-based ring pressing. Two copper rings were placed concentrically one inside the other and filled with the nanostructured material. The final rings have an inner diameter of 28 mm and an external one of 39 mm.

For the proper performance of the material, the parameters of the pressing have been carefully adjusted. Moreover, the pressing set-up has been specifically adapted to avoid oxidation and enhance the density of the material and the stability of the rings. By this, two different ways of pressing have been tested: cold press and hot press. For the cold press, the best results were found when pressing the material at 7 tonnes under an inert atmosphere. For the hot press, the best results were found when pressing at 7 tonnes, at 300 °C and under inert atmosphere. For both systems, after pressing, a thermal treatment under inert atmosphere was performed at 550 °C to anneal the material and ensure the stability of



the material when working at high temperatures. In addition, after the pressing step, all rings were carefully stored under inert atmosphere to avoid extra oxidation.

NEXTEC materials with improved efficiencies were tested at CIDETE facilities for the ring manufacture. In addition, it was possible to measure its electrical performance in the primary test bench. The two ways of pressing were also tested, arising different values for the different materials.

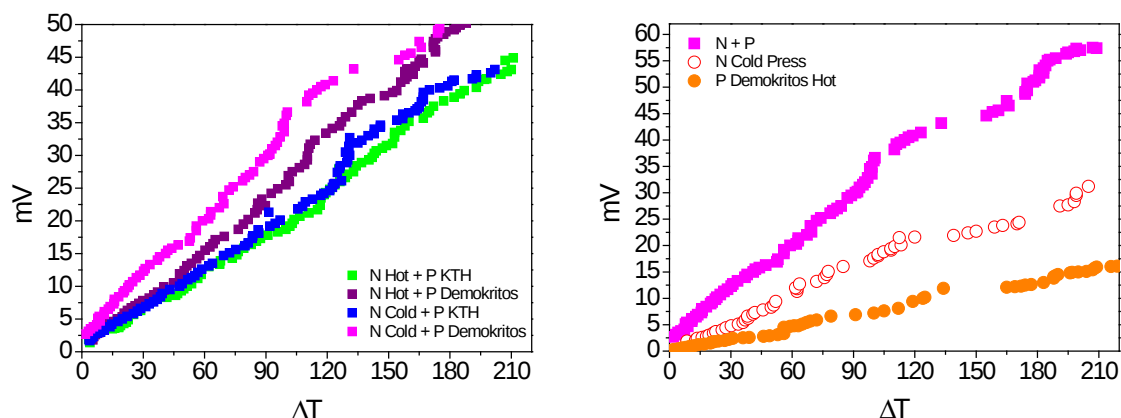


Figure 28. Electrical potential generated for materials provided by different partners in a single skutterudite ring

These measurements were crucial for the final decision of the materials for the manufacture of the final module. From all the possible combinations, the chosen materials and characteristics for the pressing were:

- N-type: material from CSIC pressed under Cold Press conditions.
- P-type: material from KTH and NCSR-Demokritos pressed under Hot Press conditions.

After the ring manufacture, the second step was the assembly of the module. Two modules were assembled during this period. The second, and final one, contained the improved materials and also an improved system for the electrical contacts. For the module **assembly was crucial to ensure the electrical and thermal contact between the rings**. In that way, additional copper rings were used for the interconnection of the rings (inner connectors and outer connectors). Moreover, to avoid short-circuit between rings, ceramic insulation rings were designed to ensure the proper conduction of the generated electricity (inner and outer insulator rings).

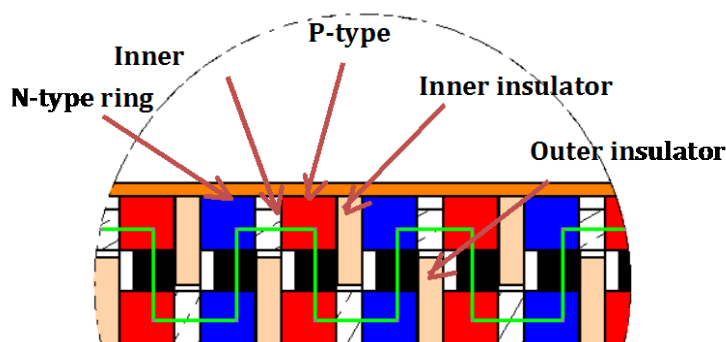


Figure 29. Pathway of the current in the new ring configurations

In addition, high temperature silver paste was used for the enhancement of the electrical connections. Thermal grease Omega 99 was applied to minimize thermal losses. The final module contains 18 N-P pairs with improved efficiency and enhanced electrical connections as shown in Fig. 30.

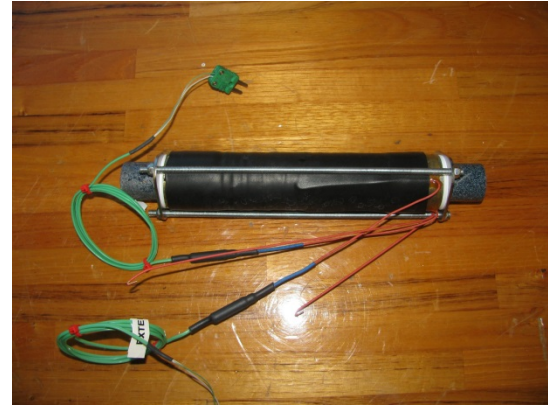
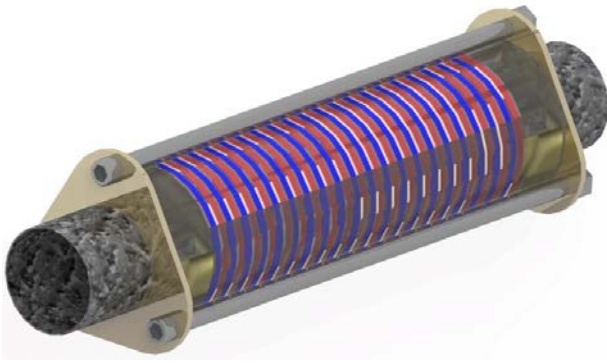


Figure 30. Tubular TEG prototype

- *Planar Modules for Energy Generation*

In order to test NEXTEC materials for energy generation, a planar module was also necessary. A module with exactly the same materials used in the ring configuration module was built. Materials from CSIC and Demokritos were pressed into round pellets 10 mm diameter and 2 mm height, under 1.5 tons using cold press conditions. Afterwards, a heat treatment at 550 °C under inert atmosphere was performed for the sintering of the material. A module of 6 pellets and 3 N-P pairs was built as a proof of concept.

- *Planar Modules for cooling Application*

A Bi_2Te_3 -based module for cooling applications was designed. Materials from KTH were pressed into round pellets 10 mm diameter and 2 mm height, under 1 tonne using cold press conditions. Afterwards, a heat treatment at 300 °C under inert atmosphere was performed for the sintering of the material. A module with 12 pellets and 6 N-P pairs was built as a proof of concept. A schematic is shown in Fig. 31.

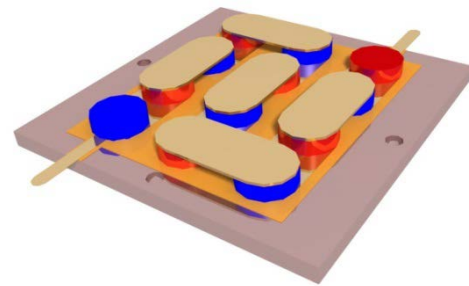


Figure 31. Schematic of planar module for cooling application

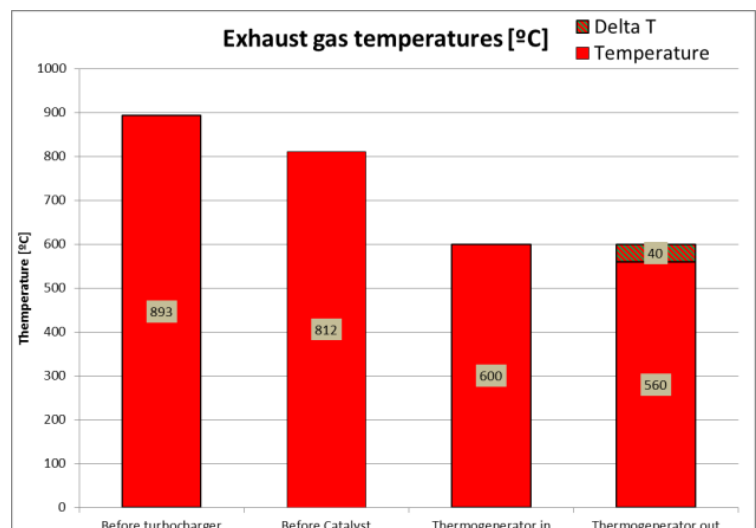
Module Testing

- *Proof of concept for Ring Configuration*

A preliminary test with a heater and a blower has shown that the first ring TEG does not give any electrical power (0mA). However, the temperature distribution and heat flow through the TEG can be measured.

Thermal power and temperature distribution: After several tests an optimal working point is found in the engine, where exhaust temperatures are as high as possible with the minimum exhaust backpressure. The engine steady state working point stays as follows:

Engine speed: 2600 rpm
 Load: 90%
 Intake air flow: 318 kg/h
 Lambda setpoint: 1
 Exhaust backpressure: 475 mbar
 Exhaust temp. before Turbocharger: 893°C
 Exhaust temp. after Turbocharger: 812°C
 Exhaust temp. before Thermogen.: 600°C



Exhaust temp. after Thermogen.: 560°C.

Water temp. in: 25°C

Water temp. out: 30°C

The temperature distribution across the entire system shows a bad working temperature for rings. With 600°C gas temperature, there is a big heat transfer loss between gas and the inner ring, and another one between the outer ring and water. In this case, the temperature gradient in the TE material is limited to a range between 53 and 143 °C. The maximum thermal power delivered to cooling fluid is 2950W. The higher center rings temperature indicates that some of the heat delivered by the gas has gone directly through water, cooling the outside zone rings.

Electrical power: Using the CIDETE test bench one ring of each type is measured. Over 200°C the current dropped dramatically and after removing the oxide layer over the copper inner ring the current returned to plausible values. Obviously oxidation caused degradation of the ring performance. However there is an initial measure using a heater and a blower with water spray for cooling. The results indicates a drop in electrical current and power over only 130°C working temperature and 45 °C temperature difference, very low value for Skutterudites, so power is very low. The origin of this drop is under investigation to clear why does it happen, but seems to be related to the oxidation layer found during the one ring measurement.

- *Testing planar modules for energy conversion*

The MTEC was used to characterize a range of commercial and prototype modules. As an illustration, we discuss results for a commercial module (Bi_2Te_3 from HiZ) whose open electrodes must be covered with an electrical insulator. The choice of insulator affects the thermal resistance and hence the optimal design of a TE system in an industrial application. Fig. 32 compares the performance with kapton foil, Al_2O_3 wafers and Al_2O_3 plus thermal grease as a function of applied pressure for fixed cold-side temperature of 85°C and $\Delta T = 140^\circ\text{C}$. Although the thermal-to-electric conversion efficiency is the same for all three insulators, the lower thermal resistance of Al_2O_3 leads to higher heat flux and hence more power generation. Adding thermal grease enables the same performance to be obtained at lower applied pressure, which is mechanically easier to implement in industrial applications.

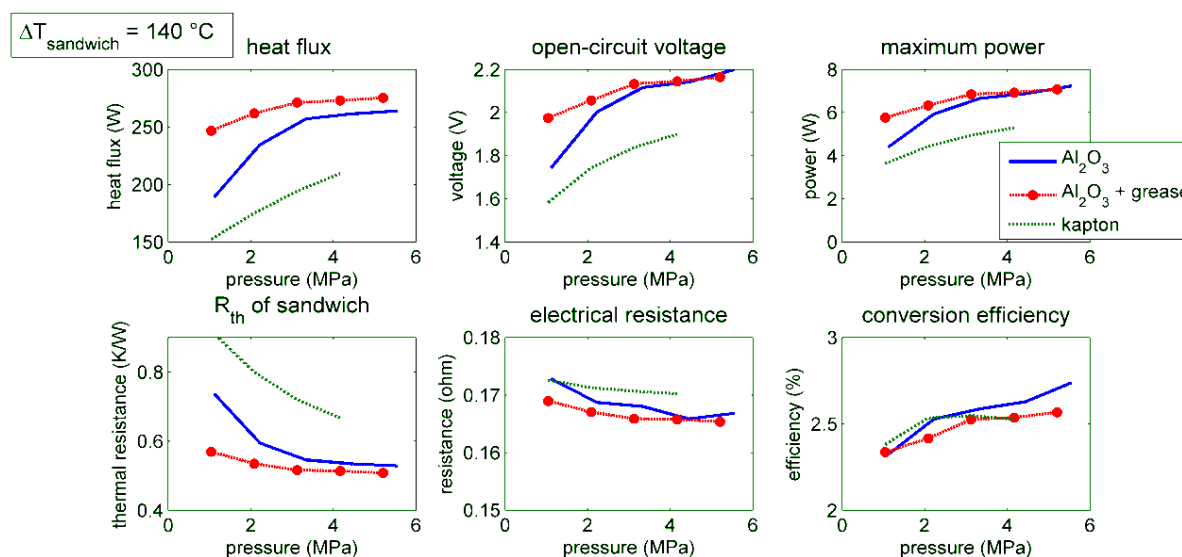


Figure32: Properties of a HiZ-module insulated with Al_2O_3 wafers (blue lines), Al_2O_3 wafers and thermal grease (red lines with dots) or kapton foil (dashed green lines). (Source: Siemens)

The partners Fraunhofer, NPL and Panco all have test benches for TE modules (pre-existing NEXTEC) and agreed to perform a round robin with Siemens with three different modules: Commercial Bi_2Te_3 , prototype PbTe from Hi-Z (up to 550°C) and prototype half-Heusler from Fraunhofer IPM (up to 550°C, developed separately from NEXTEC). The same electrical insulators and graphite foils were used by all partners, but the

applied pressure and the cold-side temperatures were necessarily different due to the different constructions of the test benches. The results showed excellent agreement between the partners for the voltage as a function of ΔT but an unexpected scatter in the electrical resistance, which needs to be clarified. As expected, the greatest variation is in the challenging measurement of thermal resistance and hence conversion efficiency, (Fig. 33).

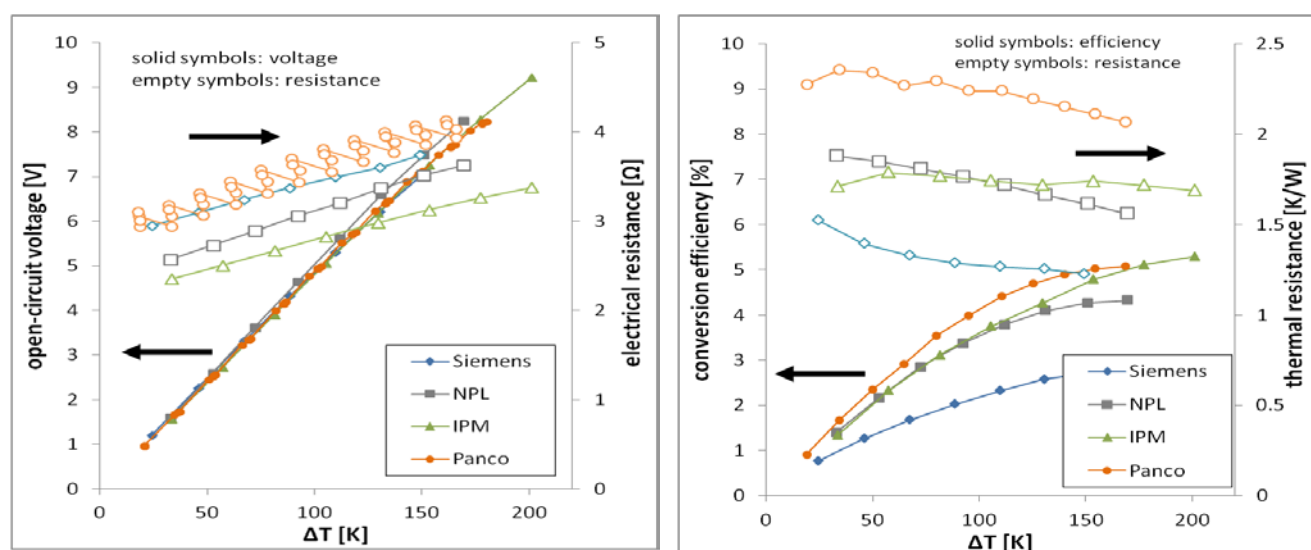


Figure 33. Example results of the round robin for planar TE modules, for a commercial Bi_2Te_3 module.

Siemens also used the MTEC to characterize the planar skutterudite module developed by Cidete. The open-circuit voltage V_0 was extremely low and the internal electrical resistance very high compared to what would be expected from the measured material properties of the skutterudites from CSIC and Demokritos. Increasing the applied pressure from 0.1 to 1.1 MPa brought a marginal improvement in V_0 , from 41 to 59 mV, but unexpectedly the resistance increased from 99 to 134 Ω (the module hot side was held at 230°C and the cold side at 40°C, so $\Delta T = 190^\circ\text{C}$). When ΔT was increased to 320°C V_0 increased to 110 mV but the resistance rose dramatically to 730 Ω . The maximum electrical power generated by the module is $<10 \mu\text{W}$ at all ΔT , which is far too low for any application. The poor performance of the module is under investigation to understand if it was due to the properties of the skutterudites or other aspects of the module design such as the joining technology.

Measurements with the application-oriented test bench reveal how other system components affect the performance of a TEG. The typical results of Fig. 34 show excellent thermal contact between the modules and the cold plate heat exchangers, whereas the module hot-side temperatures are significantly below that of the hot gas. This means that for a given industrial source of hot gas more modules are needed in order to extract a given amount of thermal energy and hence generate the desired electrical power, which significantly increases the capital costs per watt. The system performance was compared for gas heat exchangers made of steel, copper or aluminum, in the latter case with several designs of the heat exchanger fins. Taking into account the heat transfer, the gas back-pressure and cost / manufacturing issues, aluminum fins gave the best overall performance.

- *Testing of planar modules for cooling application*

Cidete prepared a module of nanostructured $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ material delivered by KTH. The module has 12 legs, i.e. 6 pairs of p and n type. The single pellets have a diameter of 10mm. The nanostructured BiTe for the cooling module has shown reasonable XRD pattern, even after storage time. However, the optimal pressing conditions have not yet been established for the nanopowder. Analysis of Seebeck coefficient of the pressed pellets with the PSM has shown a reasonable Seebeck coefficient of around $170 \mu\text{V/K}$ for the p-type, but the homogeneity was poor. The Seebeck coefficient of the n type pressed pellets was very low, around $-10 \mu\text{V/K}$, with some spots of higher values, but also spots of almost nonconductive material and generally poor homogeneity (Fig 35).

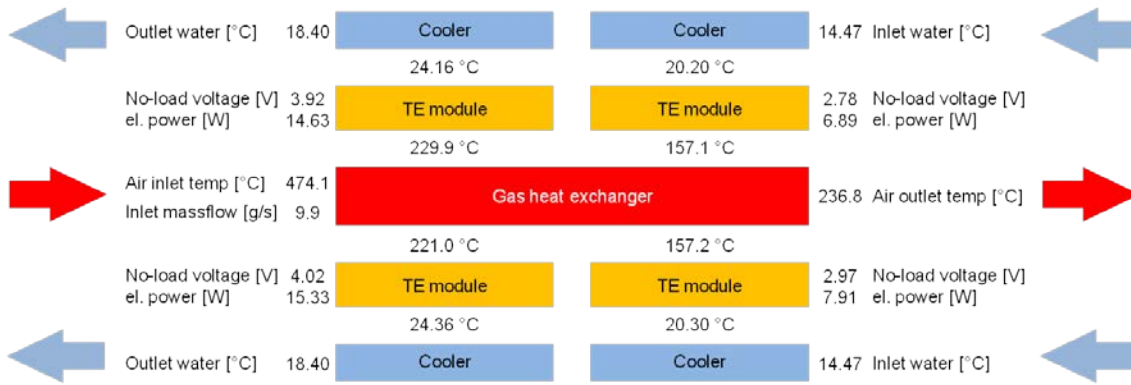


Figure 34. Example values of the parameters measured by the application-oriented test bench and their schematic relationship. The total electrical power is 45 W and the back-pressure in the gas is 3 mbar. The coolant flow-rate is 5 l/min. (Source: Siemens)

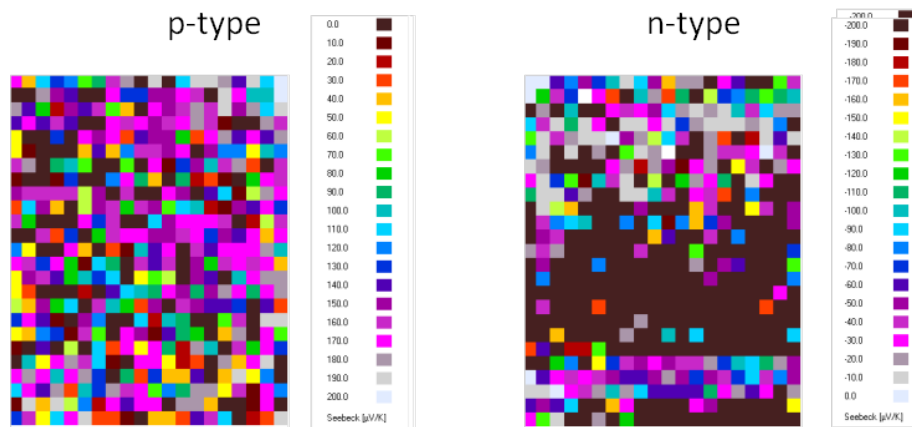


Figure 35. Spatially resolved room-temperature Seebeck coefficient of the Bi₂Te₃ pellets fabricated by Cidete from the KTH nano-structured powder and measured by Panco.

This indicates that the pressing conditions have to be improved for handling the nanopowders, as e.g., hot pressing instead of cold pressing, temperature and pressure variation, atmosphere and potentially pre-agglomeration of the nanostructured powder. This could be a complete work package in a following project. With these pellets it was rather difficult to build a module with reasonable cooling power, which was confirmed with a measurement in a modified TEG testing unit.

- *Simulation tool for TEG system*

In an industrial TEG a large number of TE modules can be arranged along each of several parallel streams of hot waste gas. The configuration of the generator must take into account not just the thermal-to-electric conversion efficiency but also the total electrical power produced and its voltage, the power produced per module (which relates to the capital cost per watt), the energy needed to pump the coolant water and the back-pressure due to the hot gas heat-exchangers. In order to develop industrial applications of TE modules these quantities must be simultaneously optimized, so Siemens developed a system-level simulation tool in Matlab which calculates how they depend on parameters of the system design, e.g. the number of modules thermally in series along the gas stream or the coolant flow rate. The properties of the TE modules, gas heat exchangers and coolant heat exchangers are read in from data-files, and system design parameters can be automatically varied in order to determine the optimal configuration. The model is flexible enough to simulate a TE generator based on either cylindrical modules like the Cidete design or planar modules, which are the current commercial standard. The model can be configured to resemble Siemens' application-oriented test bench, which enables its predictions to be experimentally verified. This is particularly useful for the hot gas heat exchangers for planar modules, since no published data could be found in the relevant regime of temperature

and air mass flow rate: their properties were calculated with fluid dynamics simulations and could be confirmed by comparing the results to the experimental measurements.

Conclusions and outlook

Siemens invested considerable effort into establishing test-benches for planar TE modules, validating the reliability of the test-benches and characterizing third-party modules (both commercial and prototype) for comparison with NEXTEC modules. The MTEC showed good reproducibility for repeat measurements, which enables systematic studies for example of how sensitive module properties are to applied pressure or to the cold-side temperature. The round robin with similar test benches at Fraunhofer IPM, NPL and Panco showed that absolute values measured by the MTEC are accurate for electrical properties (open-circuit voltage, module internal resistance) but underestimates the thermal resistance and hence the thermal-to-electric conversion efficiency by at least 30%. This is a significant measurement error, because it means that module performance appears to be worse than it is, which could cause Siemens to inappropriately reject a potential industrial application for a TE generator. In future work, Siemens will develop and test hypotheses about the source of this error in cooperation with the other round robin participants. Furthermore, the partners will fully analyse the round robin results and publish them as a journal article.

Siemens successfully developed the application-oriented test bench and considerably improved it over the course of the project, so that it is possible to carry out fully-automated measurements of how modules perform under realistic application conditions, albeit on a small scale. Here the focus is on system integration, and tests performed during NEXTEC gave valuable insight into the performance of various hot gas heat exchangers. In conjunction with the simulation tool, which Siemens developed for TE generation systems the test bench can support the development for a large-scale prototype generator. For future work the test bench should be upgraded with a more powerful heater in order to simultaneously achieve high gas mass flow and high gas temperature, and the core could be lengthened to contain more pairs of TE modules. Overall, Siemens developed test benches, simulation software and a general understanding of key issues which put it in a strong position to evaluate industrial applications of TE generators using third-party commercial or prototype modules.

The planar skutterudite module developed by Cidete showed very poor performance, much worse than that expected from the properties of the TE legs. (Note that the successful round robin of the test benches indicates that Siemens' measurements of the module performance are reliable.) Considerable development work is necessary to identify the causes and eliminate the engineering problems.

The cylindrical TEG designed by the NEXTEC project for automotive applications has achieved several important goals. The novel ring configuration is a completely new design not based in soldered junctions, not reliable at so high target temperatures, but in mechanical junctions. It makes the electrical contact between rings very surface interface dependent, and that has led to a high engineering challenge.

The time after demonstrator fabrication has not been enough to solve all the related problems found during measurement and testing of the ring demonstrator. Indeed, several additional goals have to be taken into account. Some of them have been solved from the first demonstrator prototype to the second one, others have promising solution proposals and others remain still unsolved. In addition to the original goal of good TE material characteristics, a number of additional challenges at the module-level became clear. In the radial direction these are mainly thermal and include the poor heat exchange between hot gas and the copper tube, the high thermal insulation introduced by the enamel layer, the thermally insulating plastic used to protect the rings from water and the thermal resistance caused by oxidation. In the axial direction the challenges are mainly electrical and include the tolerance to connect copper rings without touching the skutterudite, the need for axial pressure to improve contact and problems caused by outer grease penetrating between rings. The module still needs a further engineering optimization to make use of the good quality of the powder obtained. The ring design is a new configuration, although is superior to conventional/current module configuration, still needs some modifications. Nevertheless, all the information taken during the project has been really useful to increase the know-how of all the project members.

WP5: Life Cycle Impact Assessment

WP5 deals with the Life Cycle Assessment (LCA) of the new TE materials and modules developed. The WP has different tasks related to LCA and characterisation and toxicity evaluation of nanomaterials used. A LCA

study was performed to assess the environmental impact of nanostructured TE modules developed. As planned in the DoW, LCA was done following the methodology from the ISOs 14040 and 14044 but adapting it to the project goals and the characteristics of nanostructured materials. The methodology has four interrelated steps: goal and scope definition (task 5.1), life cycle inventory (task 5.2), life cycle impact analysis (task 5.5), and interpretation of results (task 5.6). The software Simapro was used for this analysis. The tasks were performed according to plan without major deviations. The two LCA deliverables (D5.1 and D5.2) were delivered according to the planned schedule.

Goal and scope definition

The goal of the LCA was to assess the potential environmental impacts of TE modules during their entire life. The LCA study was focused on the use of skutterudites (doped CoSb₃) nanomaterials in power generation systems applied to automotive industry.

The functional unit serves as a reference unit to be considered along the life cycle. The functional unit proposed for this study was: A functional TE module system used for power generation in an automobile during its lifespan (12.5 years) in Europe.

The most relevant expected environmental benefit would come from the power generation and the resulting saving of fuel, which should be quantified with prototype testing carried out within NEXTEC project. Therefore the reference flow was defined as: Energy generated by a functional module-based system for power generation in automobile applications during its lifetime.

The most important impact of the LCA study is at the knowledge level, since it defines the environmental drawbacks and advantages of this emerging technology from the very beginning of research stages. This knowledge should allow the strategic management of research activities, by assessing the development of new materials and proposing improvement measures.

Life Cycle Inventory (LCI)

LCA inventory was done gathering all relevant flows (inputs/outputs) of the different sub-systems. The processes analysed were: synthesis of SKT, manufacturing of rings, manufacturing of TE module prototype. These processes were modelled with primary data gathered from involved partners. The life stages of synthesis of SKT (through ball milling, wet chemistry and microwave) were modelled with data provided by CSIC, KTH and NCSR. Life stages of ring manufacturing and module assembly were modelled with data from CIDETE.

Use stage was assessed in a qualitative way since testing results were not available. Use characteristics were defined with SEAT for the expected module behaviour in operational conditions. For the end-of-life stage, a probable scenario was defined taking into account the European Directive 2000/53/EC for End-of-Life Vehicles, the characteristics of the thermoelectric rings and the current statistics of waste treatment for non-ferrous automobile components in Europe.

Secondary data were used for upstream and downstream processes using LCA databases (Ecoinvent), following the quality data requisites regarding geographic, temporal and technological representativeness.

Life Cycle Impact Assessment (LCIA)

Regarding the task of Life Cycle Impact Assessment, the ILCD impact method² was used to calculate the potential environmental impacts associated to the processes modelled in the previous task. Twelve impact categories were calculated (see Figure 4).

The relative distribution of impacts during all life cycles of the thermoelectric module was calculated in order to identify the environmental hot spots. Benefits from use stage were not included in this global analysis, since the fuel savings during the lifespan of the module were not known yet.

Results represented in Figure 36 showed that the stage with highest values in almost all categories was synthesis of nano-SKT (especially for p-STK synthesised through wet chemistry). Ring manufacturing through hot press vacuum had also relevant impacts in some categories whereas module assembly had lower

²The ILCD 2011 Midpoint method was released by the European Commission, Joint Research Centre in 2012. It supports the correct use of the characterisation factors for impact assessment as recommended in the ILCD guidance document "Recommendations for Life Cycle Impact Assessment in the European context - based on existing environmental impact assessment models and factors".

impacts since it is a process quite manual and with low consumption of resources. If the module is recycled at the end-of-life, environmental savings can be achieved thanks to the recovery of copper parts of the module, which go between 19% and 0-3% depending of the impact category.

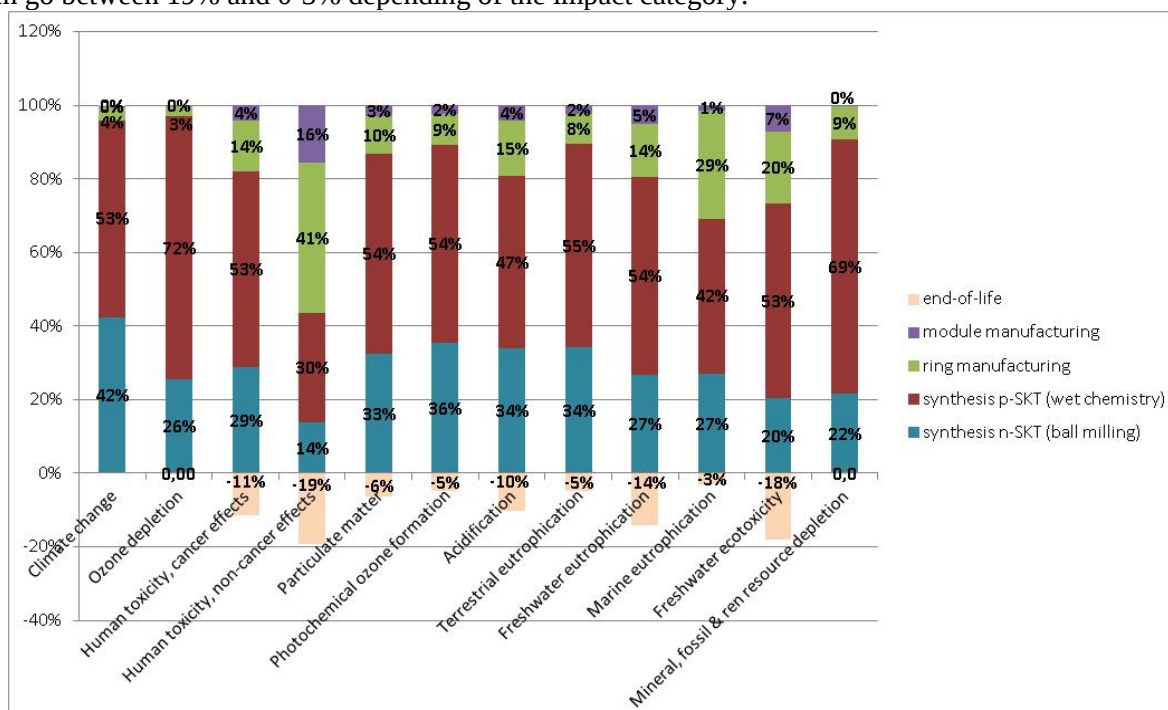


Figure 36. Distribution of impacts among the different life stages

In all productive stages, electricity had relevant contribution in most impact categories. In that sense, it should be taken into account that these processes were done at pilot scale and they may be optimized at up-scale. Substances used to synthesise materials had also relevant impacts. In that sense, toxicity and eutrophication impacts appeared to be the categories more significant in normalised results, together with abiotic resource depletion potential.

Regarding the use stage, the environmental benefits from the electricity generated by the module and the associated fuel saving during automobile operation were assessed in a theoretical way. Benefits per litre of petrol saved was calculated and preliminary results showed promising environmental improvement potential for this technology. Nevertheless a more comprehensive analysis should be done with real testing data in order to see if environmental benefits are higher than environmental impact caused during the TE module life.

A normalization analysis was done for the LCA results in order to determine the relative magnitude of the different impact categories. In the normalization stage, impact results are normalized with a common reference system (in this case Europe). Normalised results showed the highest values for the categories of Ecotoxicity, Human Toxicity and Eutrophication. Abiotic resources consumption (mineral and fuels) and climate change appeared as relevant as well.

For the most impacting stage, i.e. SKT synthesis, three different synthesis methods were assessed. The comparative analysis among these synthesis processes of nano-SKT (see Figure 37) showed that wet chemistry had the major impacts in almost all impact categories, whereas the process with lower impacts was microwave under vacuum. These results should be related to the TE properties of each material.

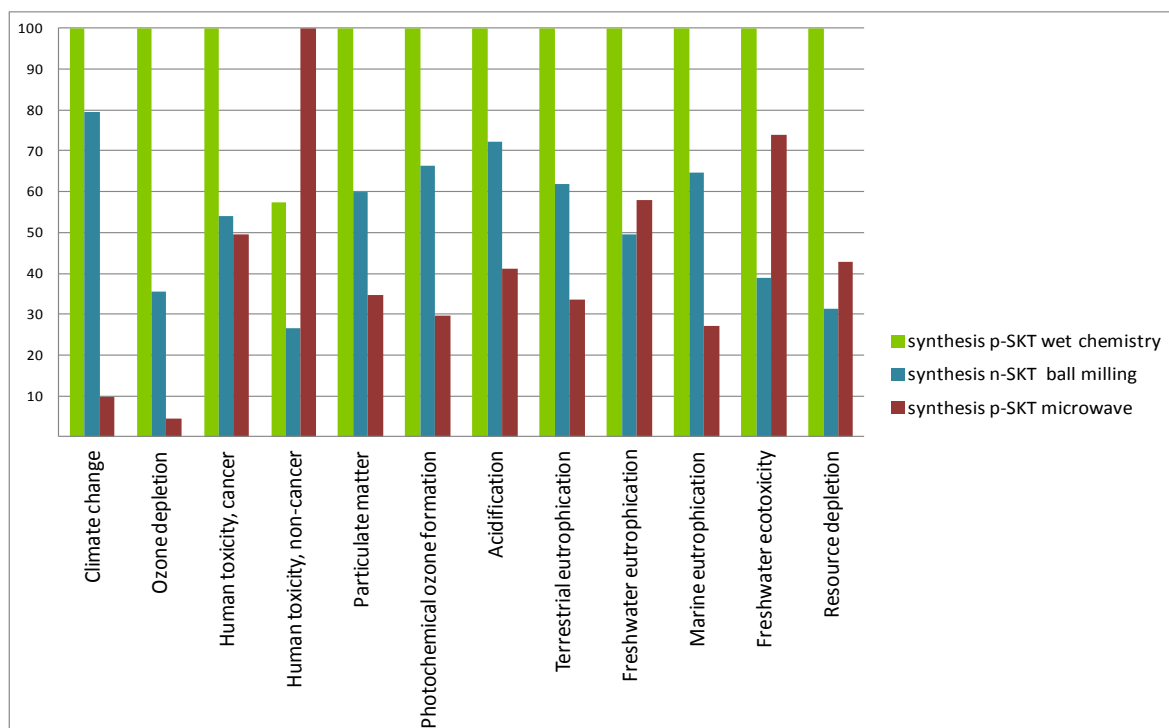


Figure 37. Comparative assessment for the three SKT synthesis processes

The results achieved by using the present framework have the following uncertainties and limitations:

Limitation of the representative and quality of inventory data for productive processes, since some data came from pilot scale process which could differ from industrial scale processes.

Limitation of the quality and reliability of primary data of some production process. Some quantitative data were based on estimations since direct measurements were difficult to do by partners involved, especially for ring/module manufacturing stages.

Limitations on the information for use stage, where simulations and testing from the project should be the basis to model the use of the module. Testing results were not available to be included in LCA analysis. Consequently, use stage was assessed in a theoretical approach.

Limitations on the information for the end-of-life stage, since the real waste treatment was unknown and a waste scenario was defined according to the characteristics of the materials and current statistics on end-of-life vehicle waste treatment at European level.

Limitations on the effect of the potential release of Skutterudites, since ideally the effect on environment and human health of Skutterudites should be integrated in LCA results. Although toxicity of Skutterudites were assessed in the project, more data on potential release and fate of these SKT would be needed in order to derive specific LCA characterisation factors for SKT materials.

Toxicity evaluation

The potential human toxicity during the different stages of the life cycle of the nanomaterials selected was evaluated and reported in a deliverable (D5.3), as planned in the DoW.

The nanomaterials finally considered in the project were the following skutterudites: $\text{Co}_0,7\text{Fe}_0,3\text{Sb}_3$ (sample code: KTH_SKUT_017), $\text{Co}_0,75\text{Fe}_0,25\text{Sb}_3$ (sample code: KTH_SKUT_015), and $\text{Co}_0,9\text{Fe}_0,1\text{Sb}_3$ (sample code: KTH_SKT_006) produced by KTH, $\text{Co}_0,8\text{Fe}_0,2\text{Sb}_3$ (sample code: NCSR_SKT_002) produced by NCSR, and $\text{Mn}_0,9\text{CoFe}_3\text{Sb}_{12}$ (sample code: p-type MASTRES) produced by CIDETE as p-type skutterdites and $\text{Co}_0,85\text{Ni}_0,15\text{Sb}_3$ (sample code: CSIC_SKT_002) produced by CSIC as n-type skutterdite.

In order to understand the hazard for human health of these materials we collected the toxicity data available in the literature for the elemental metals present in the skutterudites, and conducted selected in vitro studies with the skutterudite powders as well as with the non-doped CoSb_3 powder. This information was combined with the evaluation of the physicochemical properties relevant to toxicity in the different life cycle stages, to conclude on the human toxicity hazards in each of these life cycle stages.

- *Overview of metal toxicity.*

Cobalt and antimony are the main components of the skutterudite compounds used in this project. Both metallic elements and their compounds are irritants and sensitizers, can provoke lung toxicity, and some of their compounds are considered mutagenic and probably/possibly carcinogenic to humans by the IARC. The occupational exposure limit values for cobalt are 0.02 to 0.05 mg/m³ as 8h time weighted average (TWA) in most countries, and for antimony are set at 0.05 to 0.5 mg/m³. The other components of the skutterudites present low toxicity, except for nickel, which is a potent skin sensitizer and a skin and eye irritant at high concentrations, and it is considered genotoxic and carcinogenic. At an air concentration of nickel dust of 1 µg/m³, a conservative estimate of the lifetime risk is 4×10^{-4} .

- *Overview of cytotoxicity studies with the skutterudites.*

CoSb₃ particles (non-doped skutterudite) were cytotoxic to A-549 cells with an IC₅₀ of 267 µg/mL. The decrease in cell viability was not due to the induction of apoptosis. The different p-type skutterudites tested had IC₅₀ values for cell viability in the range of 45 to 293 µg/mL (Table 1). Differences among them seem to be related to the manufacturing process, which led to different particle sizes, rather than the final composition. Only one type of n-type doped skutterudite was selected in the project: Co_{0.85}Ni_{0.15}Sb₃ produced by CSIC. The cytotoxicity of this material was evaluated using the same assay as for the p-type doped skutterudites. The IC₅₀ for cell viability was 41 ± 13 µg/mL (Figure 4), which indicates that the toxicity of these skutterudites is similar to those synthesized by KTH.

In addition to the skutterudites we evaluated as well the cytotoxicity of CoCl₂ and SbCl₃. The IC₅₀ values obtained for cell viability were 59 ± 19 (27 µg/mL if expressed as Co) and 163 ± 60 µg/mL (87 µg/mL if expressed as Sb), respectively. These values are consistent with those reported previously in the literature for the metals either as salt or as metal. These values are also in the same range as those obtained for the skutterudites if their elemental composition is taken into consideration. This suggests that, at least in vitro, the toxicity of the skutterudites is similar to that of their main constituents: Co and Sb.

- *Toxicity evaluation along the life cycle.*

Stage 1: Materials as powder. The grain size of the materials as powder is above the threshold to consider them nanomaterials (or ultrafine dust). However, they can still be inhaled and could reach the lungs. According to the in vitro cytotoxicity tests performed in this project, the reactivity profile of the skutterudite powders is similar to what would be expected due to their chemical composition. Therefore, the in vivo hazard information available for the chemical elements of the skutterudites are considered representative for the skutterudite powders.

Stage 2: Materials after compaction into rings. After compaction, exposure by inhalation and oral ingestion is considered negligible. Exposure could still occur after extended contact with the rings. In such situation, partial dissolution of cobalt is expected to occur at sufficient degrees to cause skin irritation or sensitization. This could also be the case for the nickel used as doping agent in the n-type skutterudites.

Stage 3: Materials after coating. In comparison to Stage 2, the presence of the coating would decrease the potential for cobalt dissolution and exposure by contact. This is the stage in which the materials will be submitted to their use conditions in gas exhaust systems. The experiments performed in the project showed that the weight loss during a temperature cycle up to 750°C was below 0.5%, indicating a low risk for antimony release. In addition, being the coating intact, most of the potentially released antimony would be contained in the system and solidify again when temperature would decrease. Therefore, no (or minimal) exposure to cobalt or antimony would be expected in these use conditions. However, the integrity of the coating should be evaluated after repeated use.

Stage 4: Materials at the end of life. During the dismantling of the gas exhaust systems and separation of the copper layer from the skutterudite rings there could be direct contact of workers to the skutterudite materials and release of particles to the air.

Conclusions and Recommendations

The toxicity of the skutterudite powders can be assumed to be similar to that of its main constituents: cobalt and antimony. In addition, in the case of the n-type skutterudites, the presence of nickel can also contribute to their toxicity, in particular for people sensitized to this element. The manipulation of skutterudite powders

should be done taking the necessary protective measures to reduce inhalation and the subsequent risk of lung diseases, respiratory sensitization and carcinogenicity. Similarly, the frequent manipulation of skutterudite either as powder or as nanostructured material should be done with gloves to minimize contact with cobalt and nickel and reduce the risk of sensitization.

Project Impact

The NEXTEC project was driven by end-users requirement as identified by SEAT, SIEMENS and ELECTROLUX and spanned the scientific and engineering area: from ab-initio simulations to module fabrication through materials production and characterisation.

Its main purpose was to assess the potential benefits and the integration issues for an emerging class of materials known as skutterudite. A lot of progress has been made to understand to ideal composition and the processing techniques required producing reliable high-performing materials. While not complete, this body of knowledge is a good basis to start optimizes the fabrication of real devices. A first step in this direction has been taken and a few prototypes built and tested by the consortium. As can be expected at this stage of development, the modules do not perform according to the theoretical predications. However, the facilities and know-how to produce further modules and the facilities to test them, from manufacturing to realistic relevant environment are all in place.

In a nutshell we moved from technology readiness level 2 (TRL 2, see table) to TRL 4, with further facilities developed to reach TRL 6 or 7.

Table 7- Extract from Part 18 - Commission Decision C(2013)8631 : Technology Readiness Level

TRL1 basic principles observed

TRL2	technology concept formulated	NEXTEC starting point
TRL3	experimental proof of concept	
TRL4	technology validated in lab	NEXTEC ending point
TRL5	technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)	NEXETC exploration
TRL6	technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)	Required facilities developed in NEXTEC
TRL7	system prototype demonstration in operational environment	
TRL8	system complete and qualified	
TRL9	actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)	

New Ab-initio calculation scheme: NEXTEC project delivered a series of ab-initio simulations studying the influence of different chemical composition on TE properties. Further, the lattice thermal conductivity has been calculated using a new scheme and the results were found to be in good agreement with experimental values. The NEXTEC project has successfully demonstrated that all TE properties for these systems can be calculated reliably from first principles.

New materials: NEXTEC project produced a range of skutterudite materials, and some selected n- and p-type compositions were fabricated in large-scale (200 g to 1kg batches) for module production, which is a crucial step for industrial implementation of developed TE materials.

New module design: currently, all commercial TE modules use a planar design, as do the vast majority of prototypes being developed by third parties for new, high-temperature materials. However, thermal expansion

mismatch and heat transfer efficiency should favor a cylindrical approach; the thermoelectric elements maybe more easily assembled in this configuration as well. The project has develop unique knowledge to produce cylindrical module and hold a patent on this.

New characterisation facilities: The project developed TE measurement methods with sufficient accuracy to differentiate between materials with different compositions and structure and to provide support in the measurement of power harvested from systems in realistic thermal conditions. The test-benches developed for modules will significantly help the industrial member of the consortium, Siemens, Seat and Electrolux, in deciding whether or not to develop TE generators.

New commercial knowledge: Both within Europe and elsewhere a number of parties are developing TE modules for high-temperature applications, based on half-Heusler compounds (e.g. Fraunhofer Gesellschaft, Germany), skutterudites (Fraunhofer Gesellschaft, Germany; Treibacher, Austria and partners; Matres, Italy, and partners; Marlow, USA), oxides (TES New Energy, Japan) and other materials. Currently only a few small-scale (< 1kW) prototypes of TE generators exist worldwide, and no organization possesses the necessary systems-level knowledge to be able to develop a TE generator as a commercial product in the immediate future. NEXTEC has enabled the partners to position themselves in a favorable position in this respect. Taken together, these will help Siemens to analyze the business case for developing a large-scale TE generator for a particular industrial application based on a particular new (third-party) module. This will significantly support the industrialization of TE generators, which can potentially increase the energy efficiency of many industrial applications and reduce CO₂ emissions. Whether Siemens actually enters this market, and if so on what scale, is dependent on the future development of TE modules which are cheaper, more efficient and capable of higher temperatures than those currently commercially available, and furthermore on the development of large-scale manufacturing facilities for such modules.

New EU wide infrastructure: The test benches developed by Siemens, NPL, Fraunhofer and Panco for individual modules and for application-oriented set-ups, together with the system-level simulation tool develop by Siemens, will support future developments in several ways. The partners can independently measure the performance of TE modules developed by third parties, enabling a fair comparison of novel modules both new and aged under controlled conditions.

New technical knowledge for individual partners: Most of these impacts can be found in the previous pages, let's just mention for example the fact that Siemens used simulation tool to scale up the results of the application-oriented test bench and investigate the effects of changing system-level parameters. Siemens can also now experimentally identify critical aspects of system-level design and their impact on overall system performance, and conduct initial tests of proposed improvements.

Environmental impact: In the car industry there is actually a huge focus on reducing CO₂ emissions. This focus is basically generated by new laws and the need of a responsible and sustainable use of energy sources. However, most of the measurements which are analyzed actually have a high cost, which avoids the introduction of such new technology. Also, the carbon footprint of every new technology has to be considered. The main measure which is taken in count today to quantify the relation between CO₂ reduction and their costs i.e. Euros per gram of CO₂. In reality, most of the measures are currently around 0 and 150€ per gram of CO₂.

Considering that we can achieve a long term stable TEG for the vehicle-application, up to now we calculate that the price of such a generator would exceed 500€, basically due to material and fabrication costs. If such a generator is able to generate 200W, (our initial goal), and if 200W correspond to a saving of more or less 2.0 g CO₂, we expect a cost of 250€ / g CO₂. This is a very high value. Taking also in count that electromobility is moving fast and considerable amounts of plug-in hybrids and electric vehicles will be available in the nearest future (2020), we see difficulties for a mass application of TEGs as built in solution for vehicles, as these cars don't generate so much waste heat. And there is still a lot of investigation and engineering work to be realized to get a stable working and highly efficient module.

Even though the application of built in units in vehicles is considered as difficult, such TEGs are considered as highly attractive in production plants with a constantly temperature gradients (e.g. ovens).

The NEXTEC project simply was essential in order to be able to quantify the potential of the technology and to identify the biggest issues, which have to be resolved in order to get a stable running TEG module.

All partners intend to continue the exploitation of these new capabilities to further develop their business.

Project website accessible to public: www.eu-nextec.eu

4.2 Use and dissemination of foreground

A plan for use and dissemination of foreground (including socio-economic impact and target groups for the results of the research) shall be established at the end of the project. It should, where appropriate, be an update of the initial plan in Annex I for use and dissemination of foreground and be consistent with the report on societal implications on the use and dissemination of foreground (section 4.3 – H).

The plan should consist of:

- Section A

This section should describe the dissemination measures, including any scientific publications relating to foreground. **Its content will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

- Section B

This section should specify the exploitable foreground and provide the plans for exploitation. All these data can be public or confidential; the report must clearly mark non-publishable (confidential) parts that will be treated as such by the Commission. Information under Section B that is not marked as confidential **will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

Section A

The tables regarding A1 and A2 sections have already been updated in the online SESAME application.

Section B

The tables B1 and B2 have been updated in the SESAME application according to the EU guide lines. In addition the following detailed explanations for the tables are presented.

The exploitable foreground of the project, enlisted in table B2, can be divided in to 4 main categories/purposes. Following the subjects are explained in details their purpose, how the exploitation would be/was carried out and by whom, and further information regarding the patent status or patentability will be explained.

The main categories are as follows:

- Development of high throughput, high yield, cheap methods for synthesis of thermoelectric material for cooling and electricity generation
- Development of methods and instruments of measurement and characterization for the materials
- Development of test benches for characterization of TE-modules
- Development of TE modules in different configurations i.e. planar and ring configuration for cooling and energy generation

These 4 categories are presented individually in the following section.

Development of high throughput, high yield, cheap methods for synthesis of thermoelectric

For this purpose, KTH as well as CSIC, NCSRD and LEITAT provided different synthesis methods for fabrication of the nanostructured bulk material. The method developed by KTH was via a novel chemical co-precipitation of the metallic powders and further thermochemical processes to result in high purity nanostructured TE materials. This approach provides synthesis routes for fabrication of both n- and p-type material which uses cheaper precursor powders and has less impact on environment with lower heat consumption and far less time consumed for the final powders. CSIC developed optimized ball mill processes for fabrication of TE powders, which resulted in high purity and TE performance. NCSRD provided a novel microwave assisted metallurgical process which resulted in skutterudite material with very little amount of time and high purity. And finally, LEITAT reports a high throughput method using acetate salts of cobalt and antimony to fabricate skutterudite precursor material in large scale. Most of these methods were reported in journal publications except LEITAT, which also patented their process in Spain. NCSRD has already created a spin-off company for mass production of skutterudite powders using their developed process. The developed techniques will impact the production of good grade TE materials in large scale for the fabrication of TEGs in especially the intermediate temperature region.

Development of methods and instruments of measurement and characterization for the materials

The involved partners NPL, Fh-IPM developed several methods for measurement and characterization of different transport properties. These methods include in-situ ZT measurement, 3D Van-Der Pauw method for multidirectional transport property measurements. These methods have already been tested and prototypes of the measurements units have already been made and being marketed in scientific communities. In addition

round robin measurements have also been carried to provide a unified method for ZT measurements and several samples were tested with all these instruments in different facilities provided by Fh-IPM, NPL, CSIC as well as SIEMENS. All of these results are either reported in journal publications or used in internal advancement of the industrial partners. Many of the tools in the field of TE are home built and there have been issues in reproducibility of the data due to having no standard way of evaluation of materials' performance. The impact of these developed methods is expected to be in bringing in a more standardized approach to the TE field in order to be able to compare the results from different labs.

Development of test benches for characterization of TE-modules

Industrial partners i.e. SIEMENS, SEAT and CIDETE developed their own in house test benches for measurement of efficiency of the TE modules. SIEMENS developed a test bench for characterization of planar TE modules and provided reliable and reproducible data regarding their tests. CIDETE and SEAT created a test bench together with actual working automobile engine to test the efficiency of the modules provided by CIDETE. This test bench provides ample data regarding the working conditions and other aspects of the modules. These results were internally reported for the industrial advancement of the partners and had no further publication or patentability. The different set-up systems developed by different partners allow testing of the modules under real load conditions and identify the causes of possible failures to develop better and highly stable TE materials and TEGs. This will impact significantly a real market entry of TEGs in various fields of application.

Development of TE modules in different configurations i.e. planar and ring configuration for cooling and energy generation

Development of ring and planar modules were carried out by CIDETE, using the materials developed in the project, resulting in an international patent for the TEG. This prototype was tested on the test bench provided by SEAT (as detailed above) and further research and development is needed to troubleshoot, mass produce and commercialize the device by SEAT. This may provide a valuable energy harvesting system for automobiles and heavy road trucks, which will in turn reduce the Carbon footprint of relevant transport vehicles while increasing their energy efficiency. Further discussion on impact is given in Section on Project impact on page 37 of the Final Report.

4.3 Report on societal implications

This section is filled in online in the SESAME application.