Final Report Summary - NEAT (Nanoparticle Embedded in Alloy Thermoelectrics)

Executive Summary:
NEAT, acronym standing for “Nanoparticle Embedded in Alloys Thermoelectrics” is a research and development project funded in the FP7-NMP programme. By transforming part of the enormous amount of wasted thermal energy into valuable electricity, thermoelectric devices appear as a promising opportunity for renewable energy, even if materials performances is today one of the limiting factor of their industrial development. The applications of ThermoElectric Generators (TEGs) heat waste recovery are located in three fields, road transportation (fuel economy estimates from 3% up to 10 %, saving up to 100 Mt of CO2 emissions), industrial processes and power generation. We estimate a potential recovery of 200 TWh in Europe in these three sectors alone by 2020.
NEAT project aims at developing an innovative bulk alloy nanocomposite approach to increase the performance of eco-friendly Si based thermoelectric materials above the current state of the art values around 1 at medium (200-500 °C) and high (above 600 °C) temperatures, by considerably decreasing the material thermal conductivity.

The intentional incorporation of well controlled nanoparticles in a host polycrystalline alloy and the preservation of the nanostructure thanks to rapid sintering techniques were demonstrated on the two alloys families. For SiGe nanocomposites, we have demonstrated a 40% decrease of the cost of a good thermoelectric material by decreasing the amount of expensive and scarce constituting element. For N-Mg2SiSn alloys, a peak figure of merit value of 1.44 is obtained at 500 °C reaching the highest value ever reported and ZT values below 400 °C extremely high, opening interesting opportunities for low temperature energy harvesting applications using an eco-compatible material.

The NEAT approach was sustained by a strong development of accurate transport models, using ab initio computations, which were validated using thin film models systems grown by Molecular Beam Epitaxy. We have achieved multilayered Si/Ge structures with tunable thermal conductivity values well below the alloy limit (4 times lower), and have theoretically demonstrated the crucial role of interdiffusion in lowering the conductivity below what could be expected for superlattices with abrupt interfaces. The validated theoretical models played a major role, in the understanding of the mechanisms at stake, and in the useful feedbacks to experimental bulk polycrystalline materials teams. Specific cross plane Seebeck coefficient characterization set-up were developed for thin film model samples.

Several TEG key enabling technologies (substrates, fillers, chemical and oxidation barriers), assembly processes and models (thermo-mechanical and thermoelectric) have been developed leading to 4 possible TEG options. While the promising potentiality of the nano-Ag sintering assembly process was assessed through lifetime tests on representative TEGs, the demonstration of the performance increase due to nanocomposites at TEG level was not possible due to problems in the assembly process reproducibility.

Finally, a positive assessment of the technologies developed was obtained in automotive and spatial use cases, on an environmental point of view using Cost and Life Cycle Analysis, and regarding the scale-up feasibility of the processes, as 3kg batches of powders and 60mm diameter pellets were obtained with scaled-up synthesis and sintering processes.

Project Context and Objectives:
NEAT, acronym standing for “Nanoparticle Embedded in Alloys Thermoelectrics” is a research and development project funded in the NMP (Nanotechnology and nanosciences, knowledge-based multifunctional Materials and new Production processes and devices) programme of FP7. It aims at the development and demonstration of a new class of high performance thermoelectrics nanocomposites, based on eco-friendly materials.

Thermoelectric materials, when assembled in so-called Thermoelectric Generators (TEG), are an interesting technological option to harvest a part of the 15 TW thermal power dissipated each year by human activities. By transforming part of this wasted thermal energy into valuable electricity, thermoelectric devices appear as a promising opportunity for renewable energy, even if materials performances is today one of the limiting factor of their industrial development.

Until recently, the best known thermoelectric materials had peak figures of merit (so-called ZT, representing the thermoelectric performance of the material) values just above 1. Structuring the materials...
at a nanometric scale level has been proposed in the 1990’s as a path to enhance the materials performances, either by increasing the material’s power factor (product of the electrical conductivity and the squared Seebeck coefficient), or by reducing its thermal conductivity. The latter has been demonstrated, with reported ZT values larger than 2, for several types of thin film nanostructured materials. Very recently, a similar performance was demonstrated in bulk materials, by a maximum reduction of lattice thermal conductivity, adding the effect of atomic scale lattice disorder, nanoscale endotaxial precipitates and mesoscale grain boundaries to scatter heat carrying phonons in all the mean free paths range. The resulting record-high ZT value reported of 2.2 at 915K in PbTe based systems, is achieved with an approach applicable to all bulk thermoelectric materials, which is highly commendable since PbTe cannot meet industrial requirements in terms of cost, abundance and HSE.

NEAT project will develop such an innovative bulk alloy nanocomposite approach to increase as much as possible the ZT values >1 at medium (200-500°C) and high (above 600°C) temperatures by considerably decreasing the material thermal conductivity. In particular, nanoparticle inclusions and grain boundaries of the host matrix alloys will be jointly optimized in order to maximize phonon scattering at multiple length scales, without increasing electron scattering significantly.

This project is focusing on eco-friendly materials, suitable to harvest energy in the kW range and designed to operate in high thermal gradient such as the ones of automotive engines or industrial systems. It focuses on three types of nanocomposites:
- For medium temperature range (200-500°C), adequate nanoparticles (Mg2Si, others...) in n-Mg2SiSn alloy matrix will be investigated. These alloys have current reported bulk ZT values from 1.1 to 1.4 at 500°C and CEA has theoretically indicated that their ZT could be enhanced beyond 1.8 at 500°C by embedding nanoparticles.
- For high temperature range (600-900°C), adequate nanoparticles (Ge, Silicides, others...) in p and n-SiGe alloy matrix will be evaluated. SiGe alloys have proven their reliability in spatial missions. Recent theoretical predictions by CEA indicate that nanocomposites based on Ge or silicides nanoinclusions in mono-crystalline SiGe host matrix may reach ZT>2 at 900°C.
- For high thermal gradients accommodation, a graded nanocomposite of both medium and high temperature materials will be designed. This hybrid architecture will be achieved by an advanced mixing and graded temperature sintering process preserving base material nanostructures.

The concept achievement will require manufacturing process innovations enabling the inclusion of well controlled nanoparticles in a host polycrystalline alloy and the preservation of the initial architecture during the sintering. To achieve such an ambitious goal, NEAT project will focus on the following objectives:
- Produce fully tailored Ge and silicides nanoparticles (NanoDots ND and NanoWires NW) with 5nm-100nm diameters with narrow (max−min ≤ mean) and large (max−min ≥ 2×mean) size distribution, and identify optimized structural parameters;
- Develop an innovative nanotechnology to produce nanocomposite powders of thermoelectric materials with 1% to 10% nanoparticles concentration to achieve minimum lattice thermal conductivity (l≤2 W/m.K for high temperature and l≤0.7 W/m.K for medium temperature nanocomposites);
- Develop fast sintering processes to preserve the nanocomposite architecture (nanoinclusions changes in size ≤ 50% of initial size) and TE power factor (S2 nanocomposite = S2 bulk alloy) and investigate advanced graded temperature sintering process for high thermal gradient TEG;
- Find the physical limits to ZT enhancement in NEAT materials, by predictive theoretical simulation (fitting
within 20% the experimental measurements) validated by model material fabrication, detailed structural characterisation and nanoscale transport measurements;
- Assess the thermoelectric performances (thermoelectric yield targeted 15% of the Carnot yield) and lifetime (performance loss ≤ 5% after 100h annealing) through “proof of concept” TE converters optimized for heat flux transfer, as well as their compliance to operational constraints;
- Assess nanocomposites-based TEG energy pay-back, by evaluation of energetic performances, manufacturing cost and LCA in the cases of automotive and chemical plants case studies.

Project Results:
- WP1 : Nanocomposite powders synthesis

- T1.1 Nanosafety
There are two main safety issues related to the NEAT project technological developments. The first one comes from the pyrophoric Mg based alloys, which have already caused some deterioration due to inflammation of the mechanical alloying residues. Tests of the powders reactivity to the environment (water, solvents, flame, air, temperature) have been performed, and recommendations as to the ball milling procedures as well as to the storage and handling of these powders have been subsequently given.

The second issue relates to the potential nanometric size of some of the NEAT nanocomposite elements. Raw materials, host matrix and sintered nanocomposites present no risk, whereas nanoparticles for inclusions and mixed nanocomposites powders present a risk. Nanosafety considerations as well as the nature of the powders and their reactivity to air triggers that these powders should be handled in inert atmosphere in a glovebox closed environment, to eliminate any danger of inhalation or skin contact.

- T1.2 ND and NW synthesis with size and size distribution width control

Appropriate nano-inclusions to be incorporated into the alloys matrices were selected based on thermodynamical computations and theoretical recommendations. Among the possible nanoparticles, selection was driven with the final aim to highlight the contrast in thermoelectric behaviour of embedded nanoparticles that are/are not lattice matched and thermodynamically stable within the host matrix, and to compare the effect of different sizes.

15 types of nanoparticles (NPs) have been synthesized using either ball milling (wet or dry), wet routes (surfactant stabilized or not), or Flame Spray Pyrolysis, enabling a control on the NPs size (in 10nm range) and size distribution (Figure 1).

- Ball milling route has been investigated for silicides nanoparticles production for SiGe and Mg2SiSn alloys. In the cases studied, the targeted phase formation during high energy milling was incomplete, and thermal annealing was required to finish the synthesis, triggering a significant growth of the particles mean size to reach nanoparticles size larger than the optimal size predicted by preliminary theoretical computations. Notwithstanding, it was possible to obtain two types of real nanometric silicide nanoparticles (20nm mean size) by dry and colloid milling of metallic nanoparticles sourced by commercial route (typically below <1µm), incorporated into SiGe host matrix alloys, and undergoing silicidation during subsequent processes. In the case of MoSi2, the resulting nanocomposites have shown a strong NEAT effect in the case of low Ge content host matrix phase.
- Wet routes were used as an alternative to ball milling to obtain mono-dispersed nanoparticles in the good size range (typically 10nm). In some cases, the preparation route can be tuned to vary the size of the particles by changing surfactant/reductant ratios, which is interesting for the project approach. Routes have been abandoned due to low yield and low likelihood of a suitable scale-up route being found. Successful processes have been developed for the production of metallic precursors, to be post-processed into the targeted nanoparticles before or after blending into the host, and for the direct production of the desired composition (MoSi2 using SHS). A negative impact of potential organic residues present in some cases is suspected but not formally demonstrated.

- Finally, Flame spray pyrolysis has also been a first choice technique to process nanoparticles in the below 10nm range. 6 different nanoparticles have been produced with the possibility to vary the mean size and a narrow nanoparticle size distribution. In this case also, the targeted nanoparticles were obtained either directly (in the case of oxides) or through post-reduction steps (metallic nanoparticles). Both approaches have been successful, with trickier process optimization to obtain a pure phase in the latter. In this case, XRD and HRTEM characterization was used to follow the post-processing efficiency (Figure 2).

- T1.3 Nano- to microcrystalline synthesis of alloy host matrix powders

- SiGe host matrix alloys:

CEA has developed Si1-xGex host matrix powders based on planetary ball millers. Silicon germanium alloys were ball-milled by batches of 50g, using B and P as respectively P and N dopants. First concentration developed was Si0.8Ge0.2: Powders present morphological characteristics such as large agglomerates mean size (30µm), composed of small grains including small particles estimated at 10 nm in size by DRX and measured as 40-80nm sized by TEM (Figure 3). EDW and TEM analysis on the raw powders revealed presence of an oxide layer at the surface of the grains, which impacts the final thermoelectric properties. Thus, investigating the process reproducibility, batch to batch differences were at first attributed to ill-controlled dopant incorporation in the matrix during milling. However, subsequent experiments revealed that the oxidation of the precursors/powders is responsible for the materials properties discrepancies. A study of the impact of oxygen content in the environment during synthesis and pre-sintering steps has been completed on Si0.8Ge0.2 alloys with the establishment of a correlation between the frequency and size of silica nodules in the microstructure and the measured thermoelectric properties. The full understanding of the phenomenon at stake was completed: We observe that, the more and the smaller the nodules, the higher the ZT. With 20nm mean size silica nodules a ZT of 1.02 was obtained for Si0.8Ge0.2 N-type alloys at 700°C which is very similar to the reported 1.1 value of MIT for the same concentration alloys but with nano-grains (Figure 4). This increase of ZT is partly related to a decrease in thermal conductivity, due to nanoscale effect. Another part is related to dopant segregation at grain boundaries which has a large effect on electrical properties. This result is a confirmation of the NEAT effect, even if the nanometric silica nodules are not added per-se via a controlled ex situ route.

In a second time, Ge concentration of the SiGe alloy was decreased to 8%, in order to significantly decrease the host matrix alloy cost. The process parameters and dopant concentration have been optimized for both P&N type composition. For P-type, Si0.92Ge0.08B0.7 gives similar performance as the 20% Ge rich composition, reaching 0.5 at 600°C; For N-type Si0.92Ge0.08P0.7 gives ZT=0.7 at 700°C. The study of the nanoscale effect from silica nodules has also been completed in Si0.92Ge0.08 alloys and is even more striking, with an increased ZT from 0.5 to 0.7 at 700°C, fully attributed to thermal conductivity decrease (Figure 5). The corresponding microstructure analysis shows a comparable
microstructure (grain size, composition...) but with different surface fraction of silica nodules, in the order of 4.7 10^-5 nodule per nm2, in the sample with larger oxygen content and larger ZT. The silica nodules are in this case of larger size (50 to 73nm mean size) but have a clearer effect on thermal conductivity due to a larger intrinsic thermal conductivity in the Ge poor alloy. The presence of nanoscale silica nodules enables a ZT improvement around 0.2 in both composition but is expected to be difficult to control at an industrial scale. Therefore this technological route was not selected for Generation3 materials as such, even if nanoscale silica will be spontaneously present in the final microstructure.

Synthesis processes of P and N doped-SiGe hosts of both compositions (Si0.8Ge0.2 & Si0.92Ge0.08) were transferred and reproduced by the industrial partner on its in-house milling tools and scaled-up to synthesise 100g of material in 4x25g batches in each milling process.

- Mg2SiSn host matrix alloys

Optimally N doped Mg2Si1-x-ySnxSby host matrix powders were developed using ball milling. Cold-welding problems were experienced at the bottom of the jar, responsible of low yield process, and large amount of materials lost, attributed to the tricky blending of soft and hard materials together. Even after DOE optimization of the process, only ~80% of material can be recovered post-milling, at the scale of 20g/25g. This indicates the route will be problematic for scale-up as it introduces errors in the targeted composition. The powders have the following characteristics: 15µm mean size agglomerates, composed of small grains containing 80-100nm size particles (DRX and TEM characterization). A thin oxide layer composed of Mg2Si2O6 was also observed by HRTEM at the grain oxide (Figure 6).

N-Mg2SiSn alloys produced by an optimized mechanical alloying have first confirmed the state-of-the art reported performances of 0.92 at 500°C, providing therefore an excellent base for nanocomposite study. First stability tests have demonstrated the stability of the thermoelectric properties of this material with thermal cycling. The real microstructure of the material obtained has been carefully studied by HRTEM (See Figure 7 left) using a thin foil prepared in glove box to avoid oxidation of the samples (material very sensitive to air). The general microstructure shows a polycrystalline material with submicronic grains (440nm mean size) with closed residual porosities. Fine intra-grains precipitation is largely present at higher resolution. The chemical analysis reveals a precipitates composition of Mg2SiSn with a larger Sn content than the matrix. The precipitates size is 13 nm mean, with a few larger precipitates in the 20nm range. This size is lower than the computed value for the inclusions size necessary in order to have a significant thermal conductivity decrease through nanostructures (20nm). The type of nano-scale features obtained by the self-precipitation technique is fully compatible with the reduction of thermal conductivity sought in the project (inclusions <20nm as computed by WP3). Lately, a finer optimization of the SPS sintering cycle of the Mg2Si0.3875Sn0.6Sb0.0125 phase has enabled to further increase the performance, reaching a ZT parameter of the optimized material similar to the ones of the best results reported in the literature (see Figure 7 right). It has to be noted that microstructure investigations (mostly TEM) on this material are still running, and are intended to be published in the coming months. The standard and optimized materials have a similar behavior, with electrical conductivities in between that of the reported values in the state-of-the art : the large differences in the values reported is probably originating from microstructure difference. In comparison to the standard material, the optimized one exhibits a much higher Seebeck coefficient whatever the temperature of interest. This point could reflect an optimized distribution of the antimony specie in the elemental lattice. The optimized material has a much higher power factor than the standard material, whatever the temperature. The power factor values for the
optimized material are among the highest ones reported.
Due to cold-welding in the case of Mg2Si0.4Sn0.6 two alternative synthesis routes were successfully investigated, showing in both cases a better yield compatible with scale-up (>90%), and for one technique better powder characteristics (flow ability, granulometry) (Figure 8), while for the other, a better compositional uniformity, and direct match with the targeted composition. Both techniques were further studied in the frame of the scale-up studies.

- T1.4 Embedded nanoparticles in host matrix alloy grains
The incorporation of the nano-particles into the host matrix will requires first dispersion of the nanoparticles, potentially removal of the ligands (depending on the NP synthesis route) and a final thermal step to allow incorporation/inclusion via rapid sintering.
Characterisation of the quality of nanoparticle dispersion in the host nanocomposites prior to SPS (at the powder state) proved tricky. XRD investigations showed little evidence of the nanoparticle in host matrix pattern (low content typically smaller than 3%). Nanoparticles are not readily identifiable from standard TEM contrast and EDX tracking of the additive become harder to differentiate between nanoparticles or host matrix. Clearly TEM investigations are required to confirm the presence and distribution of the nanoparticles in the matrix. In off-axis dark field imagery the stronger diffracting parts of the samples with the correct alignment show up as bright spots in the image (Figure 9 left). This could be interpreted as indicating that there is a good dispersion of nanoparticles within the host. However, when the nanoparticles are lattice matched with the host, an electron diffraction of the shown particles show that most of the diffraction is coming from the host n-Mg2SiSn (same as in XRD), and that the bright spots were both potentially arising from nanoparticles and small host crystallite grain.
The first tests realized on nanocomposite systems in the first part of the project had demonstrated a small increase in ZT. One of the recommendations was to improve the dispersion process in order to avoid agglomeration. The latter study on alternative dispersion techniques finally concluded that the reference soft milling process to disperse nanoparticles inside the host matrix, while not perfect, is a very good base to start with. 60% efficiency in 20-30nm size nanoparticles dispersion has been demonstrated here for the would-be Generations 3 materials Si0.92Ge0.08 nanocomposites (Figure 9 right). The effect of reducing the nanoparticles size and Ge concentration seems by now of far larger importance in the improvement of thermoelectric properties than dispersion processes.

- WP2
- T2.1 Thermodynamic computations to guide materials development
Thermodynamic calculations were carried out using FACTSAGE SGTE Database to select appropriate nano-inclusions to be incorporated into the alloys matrix. For SiGe alloy matrix, 7 types of nanoparticles have been selected for incorporation; For Mg2SiSn alloy matrix, 8 types of nanoparticles have been selected for incorporation.
Some may present slight possibilities of decomposition as foreseen in the thermo-dynamical calculations. However, based on the fact that no kinetic consideration were taken in the calculations and that sintering processes undertaken are fast, they have been anyway considered for further investigations. The selected inclusions differences in lattice and phase matching with the matrix, as well as the differences in nature (oxides/semi-conductor/metal), and density (heavier/lighter than the matrix), will enable to better understand the influence of these characteristics on the thermal and electrical conductivities of the obtained nanocomposites.
- T2.2 DOE completion for Generation 1&2 materials SPS and iH2P fast sintering - Generation 1 Materials

- Generation 1 Materials: Comparison of iH2P and SPS on Si0.92Ge0.08

For sintering ingots of Generation 1 materials, powders purchased by CEA were sintered under different conditions, and with different tools. Both, n- and p-SiGe (Si91.5Ge8P0.5 and Si91.5Ge8B0.5) nanopowders were sintered by Spark Plasma Sintering (FhG) and induction Heating HotPress (Stile) to benchmark the two techniques. On the SPS tool, a more accurate investigation of the dependence of compaction (density was measured geometrically or by Archimedes method) and crystallite size (XRD analysis) on the sintering conditions was performed. On the induction HotPress tool, the study was performed in parallel with pure Si powders as a reference. Trends show that denser samples are best in terms of electrical conductivity which is what is expected. Values obtained by 3 sintering teams are coherent with each other and with the reference process. iH2P gives excellent results on N-type samples with a maximum electrical conductivity of more than 140000 S/m, which is attributed to large grain size. A low Thermal budget (Temperature, duration) together with a low T ramping of 300°C/min allows to reduce diffusion and aggregation of nanoinclusions. However, efforts are still necessary to increase the electrical conductivity and the density, and subsequent thermal annealing was not sufficient to have tolerable thermoelectric materials. SPS gives best results on P-type with maximum electrical conductivity at 60000 S/m.

Two different Mg2Si0.4Sn0.6 types of powders coming from alternative synthesis techniques were sintered by SPS. For the first type of powders, additional phases of Mg2Si, Mg2Sn as well as pure Si and Sn were identified during characterization and lead to melting beads at high sintering temperature and holding times, requiring a careful development of the sintering cycle. The second type of powder presented no melting even for the highest temperature and holding time, and showed only a little amount of Mg2Sn without other impurity phases.

- Generation 2 Materials : SiGe alloys :

The first types of nanocomposites tested were based on Si0.8Ge0.2 host matrix, using 3 different nanoparticles, 2 lattice matched and one non lattice matched. In the first two, implementing nanoparticles in the 10nm range, a strong interaction of the nanoparticles with the host was observed, and the resulting performances were deceiving. However, the microstructure studies revealed that the inclusions are homogeneously dispersed in the alloy (even if agglomerates are also present) and that inclusions are located at the grains triple points (Figure 10). In the third case, composed of 1.3% in weight of commercial Mo nanoparticles (around 100nm mean size) into the SiGe host matrix, the resulting thermoelectric properties were a 15-20% decrease in thermal conductivity through a decrease in thermal diffusivity, and a moderate power factor reduction decreasing with temperature (-22% at RT, 0% at high temperature).

Finally a small increase of ZT (10%) has been observed at high temperature, which should be considered with caution as ZT measurements error bars are considered as ± 0.1 typically.

The return of experiment on these first systems, the impact of nanoscale silica features in the host matrix materials, the completed study of alternative dispersion systems and theoretical calculations, have oriented the second set of nanocomposites towards: more stable phases, below 20nm range nanoparticles, and Si0.92Ge0.08 host matrix composition, which has shown and was predicted to be more sensitive to nanotructuring than Si0.8Ge0.2.

A second series of experiment were therefore realized with smaller Mo nanoinclusions (20nm mean size)
than experienced before, dispersed in a Si0.92Ge0.08 matrix. The SPS cycle to sinter the obtained powders was systematically varied in order to optimize the microstructure and thermoelectric properties. A 40% increase in ZT was obtained for optimized sintering conditions on P-type sample, and comes from a division by 2 of the thermal conductivity as compared to the matrix without inclusions. The mean size of the resulting MoSi2 inclusions, formed during the sintering process, is determined as 20nm by high resolution TEM, which is coherent with the original size of the Mo NPs dispersed (Figure 11). Other nanocomposites tests were tested using a similar approach but with different nanoparticles, but in the end the MoSi2 nanocomposite was selected as the best material for a further optimization (Generation 3 materials).

- Generation 2 Materials : Mg2SiSn alloys :

The high yield synthesis method leading to pure phase Mg2SiSn alloy, was selected for further incorporation of nanoparticles to form the first set of Mg2SiSn nanocomposites. The sintering and thermoelectric characterization of Mg2SiSn nanocomposites was fully undertaken, comparing sintered host powder Mg2Si0.39Sn0.6(Sb0,01) without nano-inclusions as well as the results of the samples with 2 different nano-inclusions. The thermal conductivity did not show the expected thermal conductivity reductions by adding the nano-inclusions, as observed in SiGe samples. Finally, the highest ZT was founded for the samples without nano-inclusions, the samples with nano-inclusion showing only ZT of 0.2 at 400 C. To explain the reasons of this unexpected behaviour, TEM analysis to find out how the nano-inclusions are located in the matrix, would be necessary, but it is suspected that the oxide containing particles may have reacted with the host.

Mg2SiSn powders obtained by the low yield ball milling process, showing state-of-the-art properties, have been selected as the host matrix to test additional nanocomposites, and also to develop the self-precipitation approach as base to the optimization of Generation 3 materials for this alloy composition.

- T2.3 Architecture tuning of Generation 3 materials towards ZT>3

- SiGe nanocomposites:

Following the very promising results obtained on P-type MoSi2 nanocomposites, a similar approach was undertaken on N-type samples. For both types, the concentration of the inclusions was also systematically varied from 0 to 2% volumic, and compared to the reference host matrix. An optimum value of 1.3% vol. was demonstrated for both P-type and N-type. The power factor was found to vary little with the inclusions concentration while the maximum reduction of thermal conductivity was obtained for 1.3%vol. concentration. The best GEN3 Si0.92Ge0.08 nanocomposites with 1.3% vol MoSi2 inclusions obtained by reactive sintering have been finally compared with the best reported state-of-the-art values. State-of-the-art includes (Figure 12) : Papers reporting nanostructured N and P SiGe alloys (grain size in the range of 10-20nm mean size) with Ge compositions comparable to the one studied during NEAT; Papers reporting doping modulation in the case of N-type alloys.

For the N-type material, we clearly show that the NEAT nanocomposite has a performance equivalent to the best state-of-the-art up to 600 °C, and even better for higher temperature. The trend up to 1000 °C would have to be measured on set-up enabling measurements at higher temperature for confirmation. This result has also been obtained with Ge composition poorer than the one reported in the literature, and therefore with a less costly material. Note that the doping modulation sample shown here is a Si0.95Ge0.5 matrix with 35% of Si0,7Ge0,3P0,03 inclusion which is therefore equivalent to a 13.5% rich Ge composition.

For the P-type material, the NEAT nanocomposite is clearly more performing than its nanostructured
counterpart with similar Ge concentration, and is comparable to the best performance reported so far using 20% Ge concentration. In this case, the NEAT approach clearly demonstrates its ability to decrease the cost of a good thermoelectric material by decreasing the amount of the rare and scarce constituting element.

- Mg2SiSn alloys:
Two possibilities were investigated for the generation 3 materials based on the phase obtained by the low yield mechanical alloying process: either by enhancing the self-precipitation of nanoscale features or by incorporation of suitable nanoparticles.
Following the nanostructure study of Mg2Si0.4Sn0.6 host matrix and the demonstration of spontaneous precipitation of Mg2SiSn Sn rich precipitates, the possibility of adding a fifth component to enhance this phenomenon was studied. The adjunction of Ge was performed during the alloy mechanical alloying. The observed properties have shown a thermal conductivity decrease of 15% at all temperature compared to the phase without Ge addition. The electrical properties being similar in both samples, the difference in the final performance (ZT=1 versus ZT=0.85 at 500 °C for the process described as standard before) has been attributed to the slightly smaller size of the precipitates (in the 10nm range). However, the performances obtained are below those obtained with the phase without Ge using the optimized sintering cycle (Figure 13).

After the deceiving results obtained with previous oxide NPs, 2 nanoparticles types of metallic character were selected for the ex-situ incorporation into the well performing host. The first gave deceiving results, attributed to probable instability within the host. The second, which has a good crystal/lattice structure match gave excellent results. The electrical conductivity of the NP-added material is much higher than the one of all other materials we investigated in the 20-500 °C temperature range. The NP that are added have probably a “metallic” effect on this parameter. In the same time, the thermal conductivity of the NP-added material is the smallest one ever reported whatever the temperature in the 20-500 °C range, despite the very high electrical conductivity i.e. high electronic contribution. Microstructure investigations that are running will be critical to understand such low thermal conductivity values, especially concerning the lattice contribution (nanoparticle contribution, other phenomenon ?...). Consequently, the ZT parameter of the NP-added material is the highest one ever reported for magnesium-silicon-tin alloys (Figure 13). A peak value of 1.44 is obtained at 500 °C. Moreover, it is very important to note that in this last material developed using the NEAT approach, the ZT values at temperature below 400°C are extremely high, opening very interesting opportunities for low temperature energy harvesting applications using an eco-compatible material.

On Mg2SiSn, we have shown that optimization of the microstructure either using spontaneous precipitation or using ex-situ incorporation of NPs, enables different route of enhancement of the materials properties, either on the thermal or on the electrical side.

- T2.4 Graded temperature sintering process

Following the Generation 1&2 study on SiGe and Mg2SiSn alloys the best materials were selected. A preliminary study on the feasibility of grading the selected materials has been performed. Two main reasons have been identified as a killer for the feasibility of graded material between Si0.92Ge0.08 nanocomposite and mechanically alloyed Mg2Si0.4Sn0.6:

- Materials properties incompatibility: The Coefficient of thermal Expansion between the alloys are largely
dissimilar (around 3-4 for SiGe and around 15-17 for Mg2SiSn) : the idea of grading the materials was an attempt in mitigating the CTE mismatch to enable the combination of these two materials into a large thermal gradient TEG. However, this kind of approach requires a certain range of compatibility between the two materials, defined as the compatibility factor $s$ by Snyder. By comparing the compatibility factor of the two materials at these working temperatures, we came to the conclusion that the two materials are not compatible and therefore their association in either segmented or graded form will bring no benefit in TEG performance.

- Sintering temperature range incompatibility: The sintering cycles of the 2 nanocomposites to be associated have been optimized finely to obtain the optimal microstructure and thermoelectric properties, and to avoid samples breaking especially during the cooling step. For each of this material, the sintering window is rather narrow to have optimum TE and TM behavior. The sintering (temperature, holding time, pressure) parameters are differing largely from one material to the other. While holding time, ramping speed and pressure are in a compatible range, the temperature differs of more than 680°C between the 2. This difference in sintering temperature would be very difficult to overcome in the process of co-sintering for the following reasons : defining a thermal gradient as large on a so short distance is very difficult by varying die geometry; Mg2SiSn alloys have a melting temperature around 730-740°C, which is a killer for co-sintering with SiGe. Sintering together mixed phase will result in Mg2SiSn alloys phase exudation from the sintering die.

Because of these two reasons above, it was decided to reconsider the co-sintering activities and to use the corresponding ressources for more beneficial nanocomposites up-scale studies.

- WP3

- T3.1 Thermal conductivity of single crystal NEAT

- Model systems growth for theoretical models validation : 1D NEAT system: SiGe/Si multilayers
We have started with a simple model system consisting of Ge/Si multilayers, where we systematically varied the Si spacer thickness and Ge layer thicknesses. We fabricated a set of Ge/Si multilayers, with fixed Si spacer thickness of 6 nm and gradually increasing Ge amount per period from 0.5 to 5.5 monolayers ML. Special care was put in the control of the thickness of the grown layers, as this influences the thermal conductivity measurements. A sketch of the structure is shown in Figure 15. AFM images of the topmost surface are shown in Fig. for different Ge amounts. When the Ge amount per period varies from 0.5 to 4 ML, the sample is a planar Ge/Si multilayer (superlattice). By further increasing the Ge amount to 4.8 ML, Ge nanodots appear on the surface. The Ge nanodot density increases from $3 \times 10^9$ cm$^{-2}$ to $6 \times 10^{10}$ cm$^{-2}$ while increasing the Ge amount per period from 4.8 ML to 5.5 ML.

Because of Ge segregation into the Si spacers during epitaxial growth, the nominal Ge layer is depleted of Ge and the nominal Si spacer is enriched in Ge. So the multilayer acts as a 1D NEAT system where dense SiGe layers with high Ge concentration are separated by SiGe spacers with low Ge concentration. Cross-plane thermal conductivities of the multilayers were measured independently by differential 3ω method and time-domain-thermoreflectance (TDTR) at room temperature at JKU and University of Illinois at Urbana-Champaign, respectively. Ab initio calculations were performed by Nebil Katcho and Natalio Mingo at CEA. Quantitative agreement between calculation and experimental results are achieved by taking Ge segregation into account, as shown in Figure 16. Ab initio calculations reveal that partial interdiffusion of Ge into the Si spacers, which naturally results from Ge segregation during growth but mostly neglected in
previous studies, plays a determinant role, lowering the thermal conductivity below what could be achieved without interdiffusion (perfect superlattice), or with total interdiffusion. This work was published in Physical Review Letters (2013).

- 3D NEAT system: Ge nanodots embedded in SiGe matrix
JKU has grown Ge nanodot multilayers embedded in SiGe matrix on SiGe/Si(001) virtual substrates (VS) and strained-SOI (SSOI) wafers. The schematic sample structures are shown in Figure 17a. The Ge fraction of the matrix was varied from 0% to 20%. Atomic-force-microscopy (AFM) measurements show Ge nanodots with density of \( \sim 10^{10} \text{ cm}^{-2} \) on the sample surface (Figure 17b). Independent differential 3ω and TDTR measurements at room temperature were performed by JKU and University of Illinois at Urbana-Champaign, respectively. Although Ge nanodot multilayers are grown on three different substrates, the trends of cross-plane thermal conductivities as a function of Ge fraction of matrix are similar (Figure 17c): The thermal conductivities of the nanodot multilayers decrease by about 20% with increasing Ge fraction in the matrix from 0% to 20%. The results from JKU experimentally validate the concept of NEAT. This work was published in Journal of Applied Physics (2014).

- Thermal transport through SiGe nanostructures: from superlattices to alloys
During the first period, it has been shown experimentally that multilayered Si/Ge structures can beat the thin film alloy limit by phonon scattering at multiple length-scales: mid-to-long wavelength phonons are strongly scattered by Si/Ge interfaces while short wavelength phonons are strongly scattered by segregation-driven alloying of SiGe around the interfaces.

The thermal conductivity of Si/Ge multilayers depends on the Ge concentration profile. From an application point of view it is thus important to assess the temperature stability of the multilayers, as intermixing may be expected to occur at sufficiently high temperatures. From a fundamental point of view, it is important to elucidate how the thermal conductivity changes during the structural evolution. Specifically, one question is whether we can suppress the interface scattering of phonons by introduction intermixing. In the second period, we investigated the structural evolution of Si/Ge multilayers after post-growth annealing by TEM and photoluminescence (PL) measurements. We then measured the thermal conductivities of annealed samples (Figure 18).

The measurement results show that thermal conductivity of Si/Ge multilayer increases with increasing annealing temperature from 650°C to 850°C. When the annealing temperature is 850°C, the thermal conductivity almost coincides with that of an equivalent alloy sample. However the TEM and PL results show that the sample is still a multilayer, but with fuzzy interfaces due to strong intermixing. The thermal conductivity then tends to saturate at the alloy value after further increasing the annealing temperature from 850°C to 1000°C. The TEM and PL results reveal that after annealing at 900°C or 1000°C for 20 min, the sample has been changed from multilayers to alloy. This work has been described in detail in D8.7. In collaboration with CEA, we want now to verify whether the ab-initio calculations are able to reproduce the experimental results. The work will then be submitted for publication in Physical Review B.

- Theoretical models for thermal conductivity of single crystal NEAT

We have theoretically investigated the effects of alloying and nanostructuring on Mg2SiSn and SiGe materials. The calculations are fully from first principles, having no adjustable parameters. We evaluated the relative sensitivity of each material towards nanostructuring. This is done through the cumulative thermal conductivity function, \( K_{\text{cum}}(L) \), defined as the fraction of the heat that is carried by phonons with
mean free paths shorter than \( L \). The length \( L_h \) at which \( K_{cum} = 0.5 \) gives a measure of the nanostructure size needed to reduce the thermal conductivity to half of the bulk value. Thus, \( L_h \) is a marker of how sensitive a material is towards nanostructuring.

We find that Mg$_2$SiSn is less sensitive than SiGe, but more sensitive than PbTe, upon nanostructuring. \( L_h \) is \(~300\) nm for SiGe, \(~20\) nm for Mg$_2$SiSn, and \(~5\) nm for PbTe. We have also calculated the thermal conductivity of nanowires made of Si, C, and Mg$_2$SiSn, as a further validation of the cumulative curve predictions (Figure 19).

We have also found a correlation between thermal conductivity of the pure phases, sensitivity upon nanostructuring, and sensitivity upon alloying. As shown in the figure below, materials with high bulk \( k \) are more sensitive to alloying and nanostructuring. This means that in general it is easier to improve a mediocre thermoelectric than a good one. The main message stemming from this is that nanostructuring can help replace toxic or expensive compounds, by improving on cheaper, non-toxic ones, which had not been previously considered to be interesting thermoelectrics.

SiGe nanostructures are an ideal system to study the effects of nanostructuring on thermal transport. For thermoelectric applications, it is essential to determine, for a given atomic composition, the distribution of the atomic species that minimizes the thermal conductivity. With this idea on mind, CEA has computed the thermal conductivity for two possible nanostructured systems: embedded nanoparticles and superlattices. We have studied SiGe nanostructures with low Ge content, up to 8.5%, which are the more relevant from the point of view of applications due to the high cost of Ge. The main conclusion was that superlattices are somewhat more effective decreasing the thermal conductivity, by about 15% (Figure 20).

- T3.2 Dependency of thermal conductivity in polycrystalline NEAT systems

We have calculated the thermoelectric transport properties of nanograined sintered materials. To do this, we have customized a previous code, BoltZTrap, developed by our collaborator G. Madsen. Our modification of this program consists in replacing the constant relaxation time approximation originally employed, by a constant mean free path approximation. The latter mimics more closely the actual case of scattering by grain boundaries. This allows us to treat electrical and thermal transport on the same footing, in nanograined sintered materials. We can in this way evaluate the actual ZT of the systems, under the only constraint of having small enough grains.

The effect of nanocrystalline microstructure on the thermal conductivity of SiGe alloys has been studied using molecular Dynamics simulation. Nanograins are modeled using both the Coincidence Site Lattice and the Voronoi tessellation methods (Figure 21), and the thermal conductivity is computed using the Green-Kubo formalism.

The main conclusion is that phonon transport in nanocrystalline SiGe alloys is strongly influenced by disorder scattering, in contrast with nanocrystalline Si where the boundary scattering is the dominant phenomena. This is reflected in the different dependence of \( k_{\text{ph}} \) with the grain size, nearly linear for the non-alloyed case, \( L^{1/4} \) for the alloyed one. These dependences can be easily understood via a simple analytical derivation. We have also studied a particular kind of interfaces, the [100] symmetric tilt boundaries. The influence of the tilt angle on the phonon transport properties seems to be very small, due to the main role played by alloy disorder.

- T3.3 Electronic transport properties in mono and polycrystalline nanocomposites

- Transport properties of polycrystalline nanocomposites
Theoretical analysis and interpretation of experimental results obtained on SiGe and Mg2SiSn NEAT systems, was conducted in the final 6 months of the project. It was based on the well determined microstructure (grain size, inclusions size distribution and concentration, nanosilica size distribution and concentration) and electrical and thermal properties of the sintered SiGe alloys nanocomposite (1.3% vol MoSi2 in Si0.92Ge0.08 Generation 3 materials) and that of n-type Mg2SiSnSb with self-precipitation. We elucidate the different carrier scattering mechanisms that determine electronic and thermal transport, and link them with the measured results. This permits us to know how far we are from completely optimized systems, and to obtain insights about the physics behind the measurements.

First, we have been able to estimate the optimal doping needed to maximize the samples ZT at different temperatures. More importantly, we have also been able to extract the carrier mean free paths and their different contributions. Using them, we have unveiled that molybdenum silicide nanoparticles decrease carrier mean free paths much more strongly in p-type than in n-type SiGe. For n-type SiGe, the nanoparticles are almost “invisible” to electrons. This is possibly due to the larger Schottky barrier formed between the silicide and the matrix when the latter is p-doped. Nanoparticles also reduce the lattice thermal conductivity more strongly on the p-type samples, presumably due to their smaller size and higher concentration. This suggests that n-doped SiGe samples could still be improved if one could decrease the size of the nanoparticles embedded in them.

Concerning Mg2SiSn samples, the theoretical optimized Seebeck coefficient and electrical conductivity at different temperatures were computed. It showed that the phases used in the project are optimally doped to operate at 800K, but it would benefit from lesser doping if we wanted to use it at a lower temperature. A complete analysis will be possible when the complete microstructure analysis (on going) is available, using the same tools as the one used on SiGe alloys.

- Transport properties in monocrystalline thin film samples

Sample growth for cross-plane Seebeck coefficient measurement: In order to validate the theoretical models for the calculation of Seebeck coefficient and electrical conductivity in nanostructured semiconductors, JKU has grown doped single-crystalline Ge/Si multilayers on Si(001) substrates by MBE. First JKU has attempted growth of n-doped structures using an available Sb cell, but obtained poor crystal quality, due to strong segregation of Sb, which requires material deposition temperatures well below the usual ones. Due to these unsatisfactory results we have focused on p-doping, obtained with Boron. In this case, the same growth temperature used for undoped structures can be used.

After having verified that Boron codeposition does not alter the crystal quality of the Ge/Si multilayers, two Ge/Si multilayers have been grown, both consisting of 4 monolayer (ML)-thick Ge layers separated by 6 nm-thick Si spacers in each period. The number of periods was chosen to be 80 and 180 respectively. The total thickness is substantial for MBE-grown samples and the sample growth required ~3 and ~6 hours, respectively. Such relatively large thicknesses should enable precise determination of the Seebeck coefficient and also of the cross-plane electrical conductivity of the structures. The Ge/Si multilayers were grown on a 100 nm-thick Si buffer and overgrown with a 100 nm-thick Si cap. During growth, Si spacer layers, Si cap layer and Si buffer layer were doped with boron with a concentration of about 1x1019 cm-3.

AFM images of these multilayers show the presence of dots, probably because the chosen Ge thickness is close to the critical thickness for island formation.

Doping calibration and realization of ohmic contacts on p-doped Silicon

For calibrating the doping concentration in the samples discussed above, specific samples have been grown on an SOI substrate consisting of a semi-insulating 200-nm-thick Si layer, which is insulated from
the Si handling wafer by a 2 µm SiO₂ layer. Using this approach we can eliminate the current flow through the 350-µm-thick Si handling wafer, which would dominate the electrical transport between contacts placed on the sample surface. Electrical contacts on p-doped silicon samples have been realized by metal deposition of 150 nm AlSi capped with 30 nm of gold to prevent oxidation. Representative two-points characteristics showed excellent linear behavior with low contact resistance and no offset at the origin. The contacts can therefore be considered as ohmic, which is a prerequisite for the reliable measurement of Seebeck coefficient and electrical conductivity of our multilayers.

By measuring the sheet resistance of the samples, we have obtained the doping concentrations x of the two calibration samples: 1.3×10¹⁷ cm⁻³ (for the sample grown with the Boron cell at 1729°C) and 2×10¹⁶ cm⁻³ (for the sample obtained with the boron cell at 1641°C). These data are sufficient to obtain arbitrary doping concentrations. Further measurements of carrier concentration based on the Hall method are being prepared.

Measurement of the cross-plane electrical conductivity

The transfer length measurement (TLM) is a suitable way to obtain information on the in-plane electrical conductivity of a thin film. By varying the distance between two contacts on the film surface, it is possible to decouple the resistance of the film from the contact resistances. For cross-plane measurements a new but similar approach can be used. Here the cross-plane resistance of a film has to be decoupled from the substrate and the contact resistances. This can be achieved by the use of a modified TLM measurement, where not only the distance between two contacts, but also the height of the film is varied. By using the same etching recipes as for the Seebeck measurement or using multilayers with different heights multilayers with different total thickness can be realized.

- WP4
- T4.1 TE Characterization of nanocomposite materials
- Bulk TE characterization:

To set experimental procedures for bulk materials thermoelectric properties characterization, CEA has provided FhG with SiGe reference samples, characterized at CEA with similar equipments than FhG’s. Results have shown significant discrepancies between the 2 set of measurements performed on same samples. Electrical conductivities measured at FhG were 10% lower than the one measured at CEA, while the Seebeck coefficient was in the order of 20µV/K higher in FhG’s results than in CEA’s. The resulting power factor are within experimental errors. The difference were attributed to potential geometric factor of the probe (planarity, surface state), and to differences in measurements protocols (number of intermediate points, different thermal gradients used). Common geometry criterium were defined. On the contrary, diffusivity measurements show errors in the experimental error bars of the set-up.

- Model system thin film thermal characterization:

The cross-plane thermal conductivity of all thin film model systems samples was investigated via the differential 3⑱ method at IFW (and now at JKU) and further validated via the time-domain-thermoreflectance (TDTR) through an external collaboration with D.G. Cahill and J. Feser at University of Illinois. For the 3⑱ measurements, special care is paid to the fabrication of thin and high quality insulating layers via atomic-layer-deposition.

- Cross-plane Seebeck coefficient measurement: Two approaches are being employed for the measurement of cross-plane Seebeck coefficient.
- The first one was first proposed by Yang et al. A sinusoidal current with angular frequency 3⑲ heats a metal strip placed on top of the sample and electrically insulated from it. Processing steps development
have been made to obtain the measurements samples (inductively coupled plasma (ICP) etching to obtain the Seebeck voltage pad; dielectric layer deposition needed for electrical insulation of the metal pads and wires. After completing the processing steps, samples will be measured with the available 3 system. The experimental configuration will allow simultaneous determination of Seebeck voltage (through voltage oscillations at 2 on the voltage probe pad) and thermal conductivity (through voltage oscillations at 3 on the heating strip).

- The second one via thermal imaging and voltage microprobe. Within NEAT, JKU has developed an alternative method to measure the cross-plane Seebeck coefficient of thin films. The method relies on contactless heating and thermometry, which should be provided by a halogen lamp and a thermal imaging camera, respectively. The Seebeck voltage should then be measured by a metallic microtip which can be positioned on top of heated mesas by means of piezoelectric motors. The approach is sketched in Figure 22. The processing of specific measurements samples is also necessary here. The main tricky step consists in separating the multilayers from the growth substrate and their transfer onto a metallic substrate. In this way the substrate contribution can be removed since the metallic substrate (made of copper in the sketch) has negligible Seebeck coefficient, and electrical and thermal conductivities much larger than the semiconductor layer. All the related process steps used to obtain the measurements samples have been developed. The feasibility is shown in Figure 22.

- T4.2 Fabrication of proof of concept TEGs

- Oxidation protective coating for thermoelectric legs
During application under high temperature gradient, there is a risk of oxidation of thermoelectric legs inducing a thermoelectric performance decrease, so that a protection film is needed. The material class of SiC and SiOC is a desired oxidation protection material due to the formation of a passive layer of SiO2 which have the lowest oxygen diffusivity at higher temperature (> 500 °C). A protection film applied by a coating process (dip coating) has been developed for SiGe and Mg2SiSn alloys.

- A polishing at least with a surface roughness of less than 0.02 µm of the SiGe substrate enables a homogeneous precursor-derived SiOC layer after the pyrolysis. The first oxidation tests for 4h at 600 °C in air result in the increase of specific electrical resistivity of an uncoated SiGe from 8.44 ± 0.19 10-6 Ωm to 11.98 ± 0.25 10-6 Ωm, but otherwise a polished coated SiGe with SiOC show no changes in the electrical resistivity after the oxidation test (Figure 23). First oxidation tests of uncoated SiGe based material at 800 °C for up to 100h showed nearly no oxidation on surface, whereas a dense and homogeneously established 1µm thick protective coating to prevent oxidation could be installed on top of SiGe based materials. So, a protective coating preventing oxidation is not strongly needed for SiGe material.

- For Mg2SiSn alloys, SiOC surface layer could be established by dip coating as for SiGe material establishing a dense and tight layer on the surface. After pyrolysis at 450 °C cracked layers could be observed which were tightly connected to Mg2SiSn bulk material. The difference in thermal expansion is suspected to be responsible of the cracking : SiOC protective coating owns a CTE of ~4~10-6 K-1 whereas Mg2SiSn shows CTE of 20~10-6 K-1. Cracking is not related to chemical interaction of bulk and protective coating material but is initiated during cooling by large difference in thermal expansion.

- Adequate substrates for TEG assembly
During a first step, Aluminum nitride (AlN), and Alumina have been chosen as suitable substrates for TEG assembly. Direct Bonded Copper substrates are commercially available and are appropriate, especially AlN ones with good CTE match with SiGe, and high thermal conductivity, but there are more expensive
than the ones based on Alumina. Both were used as a reference for the first TEG development. In parallel, based on the thermo-mechanical model for TEGs developed in the project, other suitable substrates/connectors were selected. Two alternative substrates technology were subsequently developed at IKTS: AlN/W substrates to increase the thermo-mechanical properties match of the connection with SiGe; Poly-Si/Ag substrates, which shows the same coefficient of thermal expansion then AlN, lower values of thermal conductivity (~60W/mK at room temperature), but more cost efficiency than AlN. It also meets the requirements for TEG assembly, because it can operate in air up to 1000 °C only showing slight tendency to oxidize (establishing of thin SiO2 layer on the surface). Both substrates connections were developed using screen printing of metallic paste followed by a pyrolysis step. The manufacturer’s specification recommends using nano-Ag for bonding to Ag or Au surfaces. In the case of commercial AlN or Al2O3 substrates, the Cu surface are goldened. However, in the case of AlN/W substrates developed within NEAT, attempts to plate the W surface by the electrode-less plating of Ni/Au have been made. Adhesion problems have been observed and subsequent process optimization was necessary to reach a correct adhesion in the end. The required metallization steps before assembly were developed by IVF.

Beside TE materials oxidation mentioned before, metallization supports and brazed contacts tends also to react with oxygen at higher temperatures. During the second period, dip coating experiments with AlN-W and DBC (AlN-Cu) substrates have been carried out to see its applicability to already assembled TEGs. For AlN-W with thin Au layer for better brazing performance the precursor shows weak wetting resulting in complete oxidation of tungsten metallization supports in air at temperatures above 450 °C. For the DBC (AlN-Cu with Au layer) the wetting of precursor solution was slightly better and copper could be prevented from oxidation at higher temperatures in air (Figure 24).

- Diffusion barrier

To prevent inter-diffusion of the different metals at the interfaces within the TEG legs at the high temperatures of services, it is anticipated that a barrier material is required. The barrier material should be positioned primarily between the TE material and brazing material to prevent the metal in the brazing from diffusing into the TE material. Several material combinations are compatible as barrier materials. The use of metal silicide has shown good results as barrier materials in thin film applications at very high temperatures. A 100 nm MoSi2 diffusion barrier was sputtered on top of n- and p-doped SiGe, which were assembled in the test TEG, for further characterization. However, a default in the substrate preparation surface induced a high resulting contact resistance.

- TEG assembly process

Since the expected operating temperatures of the proof of concept TEGs are above the melting temperatures for normal solders, some form of brazing or sintered material as the interface material between the TE legs and the metallization on the substrates is required. A sintered interface using nano-sized silver particles (nanoTach from NBE-Tech, Virginia) has been selected due to its high thermal and electrical conductivity, as well as being a relatively soft material. It is often used as a die attach material in power electronics applications. The process to make the connection involves screen-printing of the nano Ag paste, the TE-legs are then attached, and followed by a sintering step in 270-300 °C. This interface is able to operate at much higher temperatures, which are theoretically to near the melting temperature of Ag at Tm = 961 °C if the joint itself is not required to withstand mechanical loads. The application notes from the manufacturer suggest that surfaces >3 x 3 mm2 do not need additional mechanical pressure during the final temperature step. Since the TEG-leg surface area is 4 x 4 mm2, which is close to the limit, tests with and without mechanical pressure have been made, and the
application of a pressure enable to obtain dense joints without any cracks.

First TEGs with AlN/Cu substrates and one with Al2O3/Cu substrates have been assembled at the beginning of the second period and shipped to CEA for the verification of thermo-electrical performance. The results obtained were encouraging, therefore validating the process selected. However, the first POC TEGs were connected to the outside circuitry via 0.3 mm diameter Ag wires that were attached to the metalized electrodes. The attachment was made using nano Ag in the same sintering step as the TE-legs. This resulted in both mechanical weaknesses, due to lack of mechanical pressure on the Ag wires during sintering, and relatively high electrical resistance in the thin wires. For this reason a new design for external connection of the POC TEGs were developed. In the new design three Ag plates (thickness 0.3 mm) are sintered between the substrate metallization and the TE-legs. The external connection is then made directly to the part of the two Ag-plates that stick out from the TEG. With the new design the connectors is subjected to mechanical pressure, at least in the area directly underneath each TE-leg, which results in higher mechanical stability. Also the cross-section area, in which DC current will flow, is increased from 0.07 mm2 to 2.7 mm2 resulting in lower stray resistance.

CEA has provided 4 60mm large pellets of P and N type Si0.8Ge0.2 to IVF for TEG fabrication. Pellets were metallized with Ti/Au and diced for the first assembly route without diffusion barrier, and diced when MoSi2/Ag metallization was applied (Figure 25). A complete screening of the different TEG configuration in terms of barrier diffusion (Ti/Au versus MoSi2) and substrates (AlN/Cu, Al2O3/Cu, AlN/W, PolySi/Ag) was then conducted, in order to select the best architecture for the final proof of concept TEGs (Figure 26 right). The first TEG geometry consists in 4 legs of size 5 x 5 x 5 mm3.

The performances of the different kinds of TEGs were studied under high thermal gradient (530°C) at CEA in order to determine the best TEG architecture to be used. The TEGs assembled with MoSi2 diffusion barrier revealed high contact resistance, which was attributed after analysis to bad surface preparation prior to the layers deposition. 2 TEGs integrating Ti/Au SiGe legs between each of the four different substrates were fabricated (Figure 26): AlN/W, Poly-Si/Ag, AlN/Cu and Al2O3/Cu. All the TEGs assembled with Poly-Si/Ag substrate broke during the wiring, probably due to thermal expansion coefficient mismatch between the substrate and the Ag connectors. The maximum electrical power (i.e Pmax) was measured on the other three kinds of TEGs. The best modules, based on DBC substrates without MoSi2 diffusion barrier, showed output power around 2W under a thermal gradient of 530°C (550°C hot side-20°C cold side), which fully matches with the expected performance considering material properties. This indicates low contact resistance, which was subsequently measured on specific samples to be in the order of 10-9 ohm.cm-2. For the final POC TEGs, AlN/Cu substrates were selected : AlN/W substrates were not used because their internal resistance was much higher (low W thickness resulting in high track resistance) and the FE simulations showed that there was no real thermal stress benefit in using W metallization. Al2O3 presents an interesting cost profile, however AlN was selected considering its better mechnical match, as subsequent lifetime studies will be conducted.

Due to sintering constraints (shape ratio of the pellets, and quantity of nanocomposite materials available), the final POC TEGs integrated smaller TE-legs (2.5 by 2.5 mm2 in section instead of 5 by 5). The TE legs height were varied from material to another in order to design TEGs with equal thermal resistance, to enable direct comparison of the performances. Six SiGe final proof of concept TEGs were assembled with reference Ge rich alloy Si0.8Ge0.2 reference Ge poor alloy Si0.92Ge0.08 and nanocomposite MoSi2 Si0.92Ge0.08. From the results obtained on these 6 TEGs, we concluded, that the assembly process was efficient in some case but not reproducible enough at this stage of the development, to be representative of the intrinsic properties of the materials used. Discrepancies came solely from internal resistance of
modules larger than the expected values in some modules, while the others showed the internal resistance and the power output equal to the theoretical models calculated from the material properties. In this condition the nanoscale effect of the material was masked by decrease in the maximum output power due to bad internal resistance \( P_{\text{max}} = \frac{V^2}{4R} \).

This problem of repeatability in the assembly process is confirmed when a complete summary of the results obtained all over the project is realized. As a whole, 30 TEGs were assembled during the second period of the project: 4 with Al2O3/Cu substrates, 3 with AlN/W, 4 with Poly-Si/Ag, and 19 with AlN/Cu. Over these 30 TEGs, half broke at different steps: during transportation, at wiring, during tests, after test during dismounting, or during lifetime tests. However, the TEGs which were assembled in the best conditions, have proven a good ability to withstand the high thermal gradient measurements. A summary of the conclusions of lifetime tests will be presented in Task 4.5.

The Mg2SiSn-based modules for middle temperature applications were also developed but not finished due to time constraints. Since only n-doped Mg2SiSn material was targeted within NEAT project, the plan was to connect three TE legs using sloped Ni interconnects plated with Au. The disadvantage of using sloped interconnects is that they are thermally conductive and will conduct some of the heat that would ideally go through the TE-legs, reducing overall module efficiency. However, this type of approach has already been used before in this case. The fabrication was based on plated Au-plated Ni interconnects and due to the lack of available material (low efficiency laboratory process and scaled-up powders available only at the end of the project), it was not possible to build one of these modules during the course of the project. However, first feasibility tests confirmed the compatibility between nano-Ag paste and Au plated Ni connectors.

- T4.3 Thermo-Mechanical properties and reliability of proof of concept TEGs
- Thermo-mechanical properties measurements

Thermo-mechanical properties of Si79.5Ge20.0P0.5 Si79.5Ge20.0B0.5 and Si0.92Ge0.08 alloys have been determined mainly as a basis for Finite Element thermo-mechanical models of TEG at Swerea IVF. Those data are needed to calculate thermal stress in between TE materials theirselves (f. e. hot and cold side of one TE leg) as well as for the interfaces of TE material and brazing zone and diffusion barrier layer. For that CEA provided IKTS with 60mm sintered samples. Specific proofs were cut in the ingots in order to measure the major thermo-mechanical, among them elastic constants (E, G, Poisson ratio), and thermo-dynamical properties (CTE, diffusivity, density specific heat). 60mm Mg2SiSn could not be characterized due to heavy cracking after polishing. Indeed, cutting was quite challenging due to high brittleness of SiGe and especially for Mg2SiSn alloys. The material properties of a S'Tile produced substrate of pure Silicon were also determined (density, heat capacity, diffusivity and thermal conductivity) to further evaluate Silicon as a possible alternative candidate for substrates. The values of thermal conductivity of silicon (20-50W/mK) were lower compared to AlN.

- Consolidating ceramic filler

To prevent oxidation and Mg-evaporation of the TE-leg material during operation some form of coating, sealing or filling material (or a combination of them) may be required. The materials that have been under consideration are ceramic and include fumed silica, fumed alumina and zirconia. The advantages of using a ceramic material is that they can withstand very high temperatures, can be shaped into the desired geometry and can be made to be thermally insulating by increasing porosity. Thermo-mechanical FE modelling have been performed in order to find the relationship between porosity and mechanical strength of the TEG design. In summary, increasing the porosity of the filler material would improve the thermal insulation properties and reduce the stress on the materials, which in turn improves reliability of the TEG.
Due to time constraints and the fact that it will reduce module efficiency, the filler material was not added to the final TEGs, leaving the TE legs exposed to oxidation risks.

- Thermomechanical models

The proof of concept TEG is developed first in order to allow for proper evaluation of the improved TE materials, and secondly to demonstrate a package reliable enough in long term operation. However, as thermomechanical simulations show, in the simplest packaging geometry, the high hot side temperature and ΔT between hot- and cold side induce stresses in the interface between the hot side substrate and the TEG legs, which could be higher than the yield strength of some of the materials involved. It is therefore important to mitigate this stress. To find where problems may occur in such designs, finite element modelling (FEM) have been performed.

The thermo-mechanical modeling has started with the collection of material properties for several candidates for packaging and interconnection material. Starting from this, combinations of different substrate materials for the hot and cold side of the TEG have been simulated. It was found that substrate materials with low thermal expansion coefficient (CTE) should be preferred. PolySi substrate is an excellent alternative on a thermo-mechanical point of view as it matches SiGe in CTE by example. The model shows that solders at the bottom of the substrate are subjected to the most energy and yield the most, with the upper solders also showing signs of plastic deformation. The maximum strain on the lower solders is 0.8% and the material can in theory tolerate this. This means that this TEG structure is potentially thermo-mechanically viable.

In a second step, two different simulation approaches have been developed to attempt to explain the thermo-mechanical behavior of a TEG with the new Ag connectors. The models were used to determine if adding the new connections to Cu/AIN/Cu and W/AIN/W substrate TEGs will significantly increase the predicted thermo-mechanical stresses. The results from both models suggest that there will be a small increase in the overall thermo-mechanical stress on the TEG models, but they predict W/AIN/W substrates should still withstand the induced thermal stresses. The simulation results still predict that the Cu/AIN/Cu substrates will not be able to withstand a hot side temperature of 650°C and a ΔT of 605°C.

In a third step, the geometry retained for the final proof-of-concept TEGs and for the assessment of the reliability of the assembly process (lifetime studies of Task 4.4) has also been evaluated based on the thermo-mechanical model. Si0.2Ge0.8 TE material was used and the legs had dimensions of 2 x 2 mm². These legs are smaller than those used previously, which increases the risk of the module breaking, as the thermal gradient will be greater. As an example, the results for load case 1 is shown in Figure 27: it shows high levels of stress on the TE legs, and low stress on the solder joints. This suggests that the most likely cause of module failure is TE leg fracture, which is currently supported by experimental observation. Experimental work and FE analysis indicates that the nano-Ag K-paste is unlikely to yield much, meaning that there will be little stress relaxation on the TE legs. There is therefore a potential for the TE legs to crack close to their interface with the solder joint and this risk is greatest for the small single-legged modules. This outcome is supported by what is observed experimentally.

- T4.4 Lifetime assessment

Three different tests were selected to verify the lifetime assessment. The test procedure was determined and first tests with commercial Modules were performed to validate the test rig and measurement devices, before the lifetime study on Proof of concept TEGs developed within the project.

- Steady state test 24h (3 x 8 h):

  The first test is the characterization of the electrical parameters at the TEM-test bench. In this test bench the hot and cold side of the module can be adjusted. All electrical parameters like voltage, current, internal
resistance and power output can be measured or calculated. With the first NEAT TE-modules all the test equipment were validated. In addition a verification of the measurement results obtained at Eberspacher with those obtained at CEA was performed and analyzed. After characterization a steady state test over 24 hours was performed.

The maximal power output decreased from 613 mW to 586 mW after 3 days at 500 °C constant temperature. The internal resistance increased from 0,058 Ohm to 0,061 Ohm. The slight degradation of the maximal power output and the increasing of the internal resistance indicate a problem at the contacts between the legs and metal connection, or inside of the leg material (Figure 28). By the inspection with the microscope a crack in the ceramic plate at the hot side was visible (Figure 24 top).

- Heat cycling test with module AIN/Cu-17 Si80Ge20

The second test was the thermal cycling test. This was a cycling test to check the robustness of the module under periodic thermal shocks. This test simulated the temperature changes in the exhaust system. In an automotive exhaust system strong dynamic temperature changes take place. So a thermoelectric module for automotive application should be able to withstand dynamic thermal shocks. Within the first 50 hours cycling time the module lost 50% of the power output. The power output decreased from 0,42 W down along to 0,07 W after 85 hours cycling time which are 255 hot cycles (see Figure 28). The internal resistance increased also dramatically. Also the AC-resistance increased dramatically after the cycling test. This was caused probably by the bonding of the legs or the leg material itself: note that this test was performed without any encapsulation to protect from oxidation. The module showed damages after dismounting. The legs and the contacts were still bonded. The ceramic plate on the hot side is cracked. The metal connection plates showed strong deformation. This indicates that a strong thermal tension took place.

- Mechanical testing cold and hot shake

The third part was the mechanical shock test. Inside of an automotive exhaust system the components were charged with different exciting frequencies. For this test a standard broadband noise signal was used. This signal was selected from the norm “LV 124 electrical and electronic components in motor vehicle up to 3.5 t- General requirements and test procedure and tests”. With this broadband noise signal the module was tested in the z-axis, the x-axis and the y-axis. In each axis the test duration was 8 hours. First test was carried out in the z-axis. After 8 hours test the module was inspected visually intact. The AC-resistance increased by a factor of 3 after dismounting. This indicates that the contact under pressure was probably ok, but after dismounting without the contact pressure the contacts between legs and contact bridges degraded. During the installation for the x-axis the module broke (Figure 28). The damage was either inside the leg or the crack took place between the bonding of metal plate of the ceramic plate and contact plate. For further shaker tests it is necessary to define the direct attaching parts like the heat exchanger on hot and cold side. The influence of the attaching parts is significant. If the attaching parts are definite new tests on the shaker are meaningful. Only shaker test with the complete TEG or TEG-Sub-module will resulting in real-life conditions. Nevertheless these current results give first information about weak points which have to be considered by further developments. Nevertheless the actual design is very sensitive to vibration in x-axis. For the further development maybe an encapsulation of the module would be helpful related to oxidation and stability.

- WP5

- T5.1 End users case studies definition
During the “End users case studies definition” a new comprehensive calculation and optimization tool was developed for dimensioning a TEG. This tool can be used to optimize mean design parameters by maximizing the electrical power output. In addition important engine power losses generated by installation of a TEG in the exhaust system are considered by a simplified algorithm. The net power output can be therefore used as an optimization tool for dimensioning a TEG.

Based on BiTe-material, this tool was validated and applied at a heavy duty application. Therefore a weighted 9 mode operating cycle was used to evaluate the power potential of a TEG in a commercial vehicle. The model considers a given space (volume) to optimize the selected parameters. Within this space it was proved to get an optimum by the developed multi dimension simulation model. By applying TE-material properties instead of TE-module properties a TE-module design has to be optimized supplementary by this calculation tool.

Due to low exhaust gas temperatures at diesel engines and the assumption to positioning a TEG downstream the after-treatment system the BiTe-modules shows the best performance by this study. Especially at low temperatures BiTe resulted in a better performance. At the design point 380W net power output was calculated for BiTe modules. For silicon based material the best performance was shown by Mg2Si0,4Sn0,6 + MnSi1,77 . The net power output at the design point amounts 224W. By looking to the Figure 29, the differences between the investigated materials are represented exemplary by one steady state mass flow operating point. Up to 500°C exhaust gas temperature BiTe will have a better performance according to this model. At higher exhaust temperatures above 500°C Mg2Si0,4Sn0,6 + MnSi1,77 will show better performance. This corresponds to general data of silicon based materials. By further material development it is most likely to increase the performance of silicon based composition in order to move the optimum working temperature for silicon based materials to lower levels by exceeding BiTe- values. For SiGe alloys, it is detected that these materials show an increasing performance curve up to 1000°C. This is useful for high temperature applications. In automotive applications higher exhaust gas temperatures are available at gasoline engines or in the case of positioning the TEG closer to the engine in the exhaust system or EGR system (exhaust gas recirculation). By these applications it can be assumed a better performance by using silicon based materials.

- T5.2 TE performance model of TEG with generation 3 NEAT materials

The preliminary performance model developed during the first period has been modified integrating the GEN3 materials, in order to design the final proof of concept TEGs, by predicting the performance of the modules depending on the materials integrated, the geometry as well as the contact resistance of the assembly process. As an example, the Figure 30 summarizes the expected benefits of the integration of nanocomposites materials as compared to the host matrix counterpart. Beyond the maximum output power and yield increase obtained with the nanocomposite, the decrease of the bill of material, by reduction of the volume of material necessary is also significant. The benefits are therefore two fold in this case.

- T5.3 Process manufacturability : Cost and Life Cycle Analysis

Cost and Life Cycle Analysis models regarding the production of different kinds of thermoelectric generators have been developed. The used method allows taking into account flows concerned with the production plant and machinery employed. These flows have been normalized and paid off with respect to the production amount of each considered component. This approach allows obtaining realistic LCA results and scores for all the materials and components or technological actions investigated, hence also for the TEGs.

A reference manufacturing process has first been defined and analysed for Mg2Si0,4Sn0,6 and
Si0.8Ge0.2 based TEGs. With respect to that, alternative (competing) technologies have been modelled, such as alternative synthesis routes, Spark Plasma Sintering versus Induction Heating/Hot pressing (iH2P), alternative substrates... In a second step, the reference models has been up-scaled to a pre-industrial scale, and definitive models taking into account the nanocomposite materials developed have been compared to the reference models.

The analysis outlined environmentally critical aspects related to the TEG structure. The wafers used as substrates are responsible for a very high contribution to the whole LCA score, both in the case of Mg2SiSn based system and, more dramatically, for the SiGe based one (Figure 31 top). This occurs independently from the technology applied to the powders synthesis and sintering, despite few differences existing between them. In the end, the result obtained for the nanocomposite system is similar to the benchmark counterparts, as a very high portion of the environmental impact is due to the employment of the AlN/Cu substrates. In comparison to the reference Si0.8Ge0.2 system the Generation 3 SiGe nanocomposite performs a lightly higher environmental impact, whereas the Generation 3 nanocomposite in the case of Mg2SiSn shows a decrease amounting to 1.25%. Also in this case a high portion (but not the highest one) of the environmental impact is due to the employment of the AlN/Cu wafers.

For each kind of investigated TEGs the LCA score has been be divided by the value of Power at optimal charge, which is a property characterizing the TEG itself thermoelectric performance. At this purpose, the Si80Ge20 system evidences the highest performance, as the Env/TE ratio shows the lowest value (6.12 Pt/kW). The nanocomposite system evidences a slightly lower performance (7.38 Pt/kW), which on the contrary is higher than the benchmark Si0.92Ge0.08 counterpart one (8.97 Pt/kW). About the MgSiSn TEGs, the very narrow gap between the benchmark and the nano based system is confirmed also normalizing the environmental performance to the thermoelectric one, as the Env/TE ratio is 215.92 Pt/kW for the former one and 210.67 Pt/kW for the latter one.

Also the Life Cycle Costing has been investigated for the benchmark and the nanocomposite systems. Cost related to Energy (apparatus employment) personnel, materials (ancillary materials, process gasses and fluids, as well as the components main constituents), scraps, unusable by-products dismantling, as well as chemicals and emission in general, have been taken into account in the modeling. In the end, the differences between these systems are negligible, masked in this case also by the DBC substrate cost (Figure 31 bottom).

- T5.4 Process scalability
During the second half of NEAT project a considerable effort has been done to validate the feasibility of the synthesis and sintering processes and equipment scale-up, at a level compatible with a potential industrial exploitation.

Concerning the availability of volume synthesis processes for host matrix and nanocomposite materials, the conclusions are the following:

- Scaling up of the mechanical alloying based processes (host matrix and nanoparticle synthesis) will require adaptation of the high energy mills available today in the industry to be compatible with these air-sensitive materials. It seems compatible with SiGe based alloys, but more problematic with Mg2SiSn.
- Scaling up of the nanoparticles synthesis based on wet chemistry or flame spray pyrolysis should not be problematic as pilot plants and industrial process already exists, even if the amount of solvents needed can be a limiting factor depending on the nature of nanoparticle to be produced.
- The two alternative routes explored within NEAT appear like an excellent technological option for the scaling of synthesis processes of host matrix materials: it has been demonstrated in the frame of the
project on SiGe alloys of 80/20 and 92/8 composition with performances equivalent or close to the mechanical alloyed counter-part, even if some adjustments are needed for the N-type material. For the Mg2SiSn alloys, it appears like the best option, even if performances are still below the state-of-the-art values (20% loss of performance compared to solid-state synthesis solutions, 45% loss compared to the best nanocomposite inside NEAT). However, the optimization is not yet finished.

As to the scalability of sintering processes, the work performed in the project showed that:
- SPS sintering processes can be scaled up from 20 to 60 mm pellets on SiGe and Mg2SiSn alloys using both powders available (Figure 32), with final performance equivalent to the small samples size. Major issues concerned mechanical integrity and narrow process windows, and have been solved adjusting the sintering cycles and tools as well as the process control.
- iH2P sintering equipment can be scaled up to an in-line production compatible tool. The feasibility of the approach will be validated in 2014 on pure silicon powders at a pilot level.

Potential Impact:

The approach demonstrated during the NEAT project relies on intentional incorporation of well controlled nanoparticles (tailored size, shape, density) in the alloy host matrix, exploring all additional degrees of freedom available to optimize the nanocomposite architecture towards high performance. This route can be applied to any other thermoelectric alloys, allowing either to reduce its cost by reducing the amount of scarce and expensive materials (as demonstrated with SiGe alloys with a 40% reduction at iso-performance), or to improve its intrinsic performance (as demonstrated on Mg2SiSn alloys). The efficiency and easiness of the latter path will strongly depend on the alloy properties: the lower the starting host thermal conductivity, the smaller the nano-inclusions size required to produce a significant impact. The theoretical models as well as the process (synthesis approaches, dispersion process and characterization) and methodology (sintering cycle optimization) are fully applicable to other thermoelectric alloys families. It has been shown, that both lattice-matched and non lattice-matched nanoparticles are efficient, and that stability or controlled thermodynamic transformation in the host is a critical point. The approach can also be adapted more generally to the optimization of other types of materials and properties, and hence shorten their development step.

The new assembly technology based on nano-Ag sintering evaluated in the project gave very encouraging results in terms of its ability to withstand high thermo-mechanical stress during lifetime tests under high thermal gradient. While this technology is already used for power electronics, its potentialities has been demonstrated at higher temperature in proof of concept TEGs and should be further studied in use cases as the one encountered in III-V components, optronic, solar or spatial applications. Alternative substrates and protective coatings developed open also opportunities in the field of device development and integration (sensors, packaging...).

By demonstrating the scale-up feasibility of eco-compatible, cheap and abundant host matrix alloys synthesis and sintering at a pre-industrial scale, NEAT has made a first step towards the building of a strong, mass-production oriented, supply-chain of the embryonic TEG industry, in the field of base material manufacturing, and TEG assembly. The TEG manufacturing activity could generate 39000 direct jobs for the only need of the automotive market, i.e. multiply by 390 the present job count. TEGs represent a real
The applications of TEG heat waste recovery are located in three fields, road transportation, industrial processes and power generation. We estimate a potential recovery of 200 TWh in Europe in these three sectors alone by 2020.

Based on the results obtained at the end of the project, we have shown that Mg2SiSn alloys could advantageously substitute conventional Bi2Te3 materials in the automotive sector starting from exhaust gas temperature of 500°C. This alloy has the adequate characteristics to address the massive automotive market, as it do not contain scarce materials and do not risk a rise in the cost of base material. It also provides an acceptable solution with regard to human health issues, as Mg2SiSn offers the key advantage of a low toxicity, compared to state-of-the-art materials. TE waste heat recovery in the case of road transportation or oil powered co-generators results in a decrease of fuel consumption. Estimates of fuel economy are ranging from 3% up to 10% depending on the available heat sources but also on system configurations. The impact of TEG technology on GHG emissions will mainly concern the road transportation sector, saving up to 100 Mt of CO2 emissions in the order of magnitude of CO2 emission by EU27 oil refining (130 Mt) or the chemical industry (89 Mt).

High ZT material in high temperature applications are highly suitable to reach the 10% to 15% conversion efficiency range, in order to change the TEG competitive position against more conventional waste heat recovery technologies. While the results obtained on SiGe alloys (matching best state-of-the-art values with lower Ge content) do not yet reach this target, it offers interesting potentialities in niche markets such as spatial or avionic applications in harsh environment, in the field of power generation (autonomous systems) or energy efficiency (thermal sensors).

- Main dissemination activities

The list of the dissemination events during the project are summarized in the Use and Dissemination of foreground section. A significant effort has been made to disseminate the project results, obtained for a large part during the second period of the project. On the whole, 7 papers have been already published or accepted in peer-reviewed journal of high impact factor, minimum 2, among which 1 paper published in Physical review letters (impact factor 7.943) and one in Journal of Materials chemistry (impact factor 6.101). 3 invited oral sessions related directly to the NEAT project, in well-known conferences (MRS, and Pacific RIM conferences). 15 oral presentations have been done, mostly in international conferences with broad scientific audience. 4 posters have also been presented in conferences. Part of the dissemination efforts will continue after the end of the project, as an example at least 2 more papers are planned presenting the latest project results.

A significant effort has also been made in the clustering of European funded projects:
The first workshop on Nanotechnologies for Thermoelectrics (NANO4TE) has been held on the 17th September 2013 in Warsaw as a host event of the E-MRS Fall conference. Organized by the CEA in the frame of NEAT, it has gathered 10 out of the 11 EU funded projects on thermoelectrics identified. Networking, clustering activities have been fostered as well as clear identification as short and middle term research and development needs for thermoelectrics. A web site for this clustering activity is currently being built in the frame of the project.
The Second workshop of the NANO4TE cluster has been held in Grenoble on the 13d of January. The objectives of this second workshop were to identify and validate the common research and innovation priorities of the different projects, and to update technical data and align the EU Nano4TE bottlenecks and priorities with other EU roadmaps (Nanofutures, EMIRI, KIC). An open session workshop has been organized in order to link EU NANO4TE needs to the nanofutures roadmap across the seven Value Chains. Finally to be aligned with the 1rts Nano4TE workshop conclusion, three main recommendations have been highlighted:
- an average ZT value up to 1 offers already some industrial application. No needs in a short term to move at a higher ZT
- the scalability from material to system proved components (along the value chain) is the main priority in short term
- durability is crucial for the industrial application in order to have a complete thermoelectric system.

The next workshop will be organized next September during the thermoelectric conference in Madrid.

A project web-site has been developed on a freeware Content Management System called eZpublish which enables an easy-to-use update of the site content. The development includes the creation of specific graphic chart for the project, thirty pages of contents, structured into eight tabs: Overview/Achievements/Publications/Partners/News/Links/Gallery/Medias. It has been delivered at the end of December at the following address http://www.neat-project.eu/ and is updated by the coordinator on a bi-monthly basis, to ensure good visibility on the web.

The project web site has been updated regularly with the consortium news, achievements and papers. The web site frequentation has largely increased since the last two years. Since the end of 2012, between 150 to 200 new unique visitors have been registered each month on the web-site.

A specific web-site for the NANO4TE cluster has also been created and published by the end of January 2014.

- T7.2 Knowledge Management activities
A survey of the IP landscape on thermo-electrics performed at the start of the project has been updated at the end of the project, to outline the latest trends in thermoelectrics development and identify the IP opportunities.

Discussions on 2 patents filling are on-going at CEA and JM concerning latest results obtained during the project.

- Exploitation of results
An Exploitation Strategy Seminar (ESS) for NMP project has been heldconjointly with the second progress meeting in spring 2012 near London (JM headquarters). The Exploitation Strategy Seminar (ESS) was held on the 20th of March. The seminar enabled to consider exploitation and IPR issues related to the project, and enable a first fruitful dedicated exchange between the partners on these matters.

A first exhaustive list of 24 expected exploitable results was identified and collectively discussed at the seminar. The characterizations of these exploitable results were fair to good at that moment. Although good and constructive exchanges took place for their understanding, there was still a need for further discussions among concerned partners on some of them for a better insight and convergence of views as to their full implementation and exploitation, in particular in what concerns the industrial applications.

At the end of the project this list was updated and accepted by the project partners, according to the project outputs. 17 exploitable results have been identified as such and have been described in the final
report adequate templates, 6 of which were considered as IP sensitive and marked as confidential, due to their high probability of exploitation. A comprehensive IPR situation within the consortium was worked out for each exploitable result and for each project partner. An overview was given in a matrix grouping both IPRs and exploitation claims. It revealed that the NEAT IPR situation is reasonable and typical of a collaborative project. The matrix shows that there is limited co-ownership situation, i.e. 4 out of the 17 exploitable results identified. This will be sorted out between concerned partners on a case by case basis as defined in the consortium agreement.

Finally, it is worth to note that CEA has created a spin-off company on the 7th of January 2012, based on its background on thermoelectrics. This company, counting today 6 persons, is not a direct result of the NEAT project in itself; however, there is a common understanding between this company, named HotBlock On Board and the CEA on the potential exploitation of the NEAT project results owned by the CEA, and potentially by other partners, if there are of interest to the company.

List of Websites:

Additional information regarding the project is in the project web-site at the following url: http://www.neat-project.eu For further details, contact NEAT coordinator Dr Julia Simon at julia.simon@cea.fr.

Related documents

[ final1-neat-d8-10-23052014-figures-v2.pdf ]

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