DOE/NSF Thermoelectric Partnership
Project SEEBECK
Saving Energy Effectively By Engaging in Collaborative research and sharing Knowledge

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Dmitri Kossakovski (ZTPlus)

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Presentation
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This presentation does not contain confidential, proprietary or otherwise restricted information
Overview

Dates:
Start: January 1, 2011
End: December 31, 2014
Percent complete: 5.5%

Budget:
Total (NSF+DOE): $1,453,532
DOE share: 50% (unverified)
Funding FY11: $478,907
OSU+subcontracts: $240,411
VT: $112,093
NU: $126,403

Barriers:
• Overall program barriers addressed:
  A, B, C, D
• Barriers specific to thermoelectric generators:
  - High-zT low-cost materials made from available elements
  - Thermal management
  - Interface resistances
  - Durability
  - Metrology

Partners: Ohio State University (OSU, lead), Northwestern University (NU), Virginia Polytechnic Institute and State University (VT), ZT Plus & BSST as subcontractors to OSU
Relevance and objectives

Project goal: Develop elements for a practical automotive exhaust waste-heat recovery system that meets cost and durability requirements of the industry.

Project objectives

1. Develop high-zT low-cost materials made from available elements, specifically:
   - $zT>1.5$,
   - materials with no rare or toxic elements (Te, Tl)
2. Design new thermal management strategies, specifically:
   - Cross-flow designs, heat and charge flux normal
3. Minimize electrical and thermal interface resistances:
   - Compliant, to accommodate thermal expansion
   - High thermal conductance across interface
   - High electrical conductance across interface
4. Metrology:
   - Materials characterization
   - Thermal interface resistance measurements
   - Electrical interface resistance measurements
   - Overall system performance measurements
   - Internal check: all of the above are redundant
5. Durability:
   - Compatible with automotive durability requirements
Summary of Accomplishments/Objectives

Accomplishments
1. Personnel hired (graduate students) at OSU, NU and VT
2. Subcontracts to ZTPlus being finalized
3. Technical accomplishments are reviewed further under each objective
   1. First samples of PbSe doped with indium and with gallium made
   2. PbSe:In and PbSe:Ga measured
   3. Valence band structure of Mg2Sn investigated experimentally

Objectives (following viewgraphs outline details)
1. Materials
2. Thermal management
3. Interfaces
4. Metrology
5. Durability
Objective 1. Materials

1.1 PbSe is promising
   1.1.1 Resonant levels
   1.1.2 Nanostructuring

1.2 Mg$_2$(Si, Sn)
   1.2.1 Resonant levels
   1.2.2 Nanostructuring
Objective 1.1.1 PbSe: resonant levels

1. Accomplishment: theoretical study identifies In level in PbSe

Difficulties
- Temperature-dependence
- Too many carriers

2. Accomplishment: first samples of In-doped and Ga-doped PbSe made, and first measurements reported here
Accomplishment: PbSe-Ga and PbSe-In: Figure of Merit

ZT reaches 0.9 at 900 K.

For T>750 K, In and Ga doped PbSe exhibit higher ZT compared to optimal n-type PbTe.
Objective 1.1.2 Nanostructuring PbSe

Same bulk solid-state techniques as PbTe

Dispersed nanoparticles in samples of Sb-doped PbTe:
(A) PbTe-Sb(2%)
(B) PbTe-Sb(4%)
(C) PbTe-Sb(8%) and
(D) PbTe-Sb(16%).
1. Need details of band structure to choose the right level

1. Have band structure calculations (J. Tobola): Ag creates additional DOS in valence band

3. Accomplishment: Shubnikov-de Haas measurements on single-crystal $\text{Mg}_2\text{Sn}$ doped with Ag

Possible cyclotron masses from SdH and $E_F(S)$

$m_c (0.25\% \text{Ag}) = 0.013, 0.025 \, m_e$
$m_c (1\% \text{Ag}) = 0.005, 0.011 \, m_e$

Same result for $<111> <220>$
Objective 1.2.2 Nanostructuring $\text{Mg}_2(Si,Sn)$

Concept: use liquid encapsulation

$\text{Mg}_2 \text{Si}_{1-x}\text{Sn}_x /Y$, $\text{Mg}_2\text{Si}_{1-x}\text{Pb}_x /Y$ and $\text{Mg}_2\text{Sn}_{1-x}\text{Pb}_x /Y$ systems that melt congruently

$Y$ as element

$Y$ as compound that do not form compounds with $\text{Mg}_2X$:

- binary silicides $\text{Co}_2\text{Si}$, ...
- binary stannides: $\text{Hf}_5\text{Sn}_3$, ...
Objective 2. new BSST designs for thermal management

Heat / electrical current in cross-flow geometry
(1) reduced number of interfaces and components => reduced parasitic losses
(2) high power density materials => much smaller sizes
(3) segmentation across the specified temperature differential to maximize efficiency

Objective: adapt to high-ZT materials & reduced thickness
Objective 3. Interfaces

3.1 TE material metallization

   3.1.1 Co-pressing of metallized layers and powders during process of Spark Plasma Sintering (SPS)
   3.1.2 Post processing of annealed samples and deposition of metals using Physical Vapor Deposition (PVD) methods.

3.2 New compliant device interconnects
   3.2.1 Nanosilver
   3.2.2 New systems
Objective 3.1 TE material metallization

Direct co-sintering during material consolidation (SPS)

- 400µm layer of SnTe
- p-type PbTe from powders during Spark Plasma Sintering.
- Fe foil co-sintered with p-type PbTe

Interdiffusion and likely a eutectic structure

Issues: interdiffusion, diffusion barriers
Objective 3.2 Nanosilver interconnect packaging material

Pb-free, high-T die-attach solution:

- Joint formed below 280°C;
- Melting at 960°C;
- Thermal conduct > 150 W/m-K.

Applications:
## Properties of nanosilver sintered die-attach compared with the others

<table>
<thead>
<tr>
<th></th>
<th>Processing temperature</th>
<th>Max. use temperature</th>
<th>Electrical conductivity $10^5$ (Ω-cm)$^{-1}$</th>
<th>Thermal conductivity (W/K-cm)</th>
<th>Die-shear Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-tin solder</td>
<td>217°C</td>
<td>&lt; 183°C</td>
<td>0.69</td>
<td>0.51</td>
<td>35</td>
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<tr>
<td>Lead-free solder</td>
<td>260°C</td>
<td>&lt; 225°C</td>
<td>0.75</td>
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<td>Gold-tin solder</td>
<td>310°C</td>
<td>&lt; 280°C</td>
<td>0.625</td>
<td>0.58</td>
<td>30 - 60</td>
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<tr>
<td>Silver epoxy</td>
<td>100 – 200°C</td>
<td>&lt; 200°C</td>
<td>0.1</td>
<td>0.1</td>
<td>10 – 40</td>
</tr>
<tr>
<td>High-Pb solder</td>
<td>340°C</td>
<td>&lt; 280°C</td>
<td>0.45</td>
<td>0.23</td>
<td>15</td>
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<tr>
<td>Hysol® QMI 3555 R</td>
<td>300 – 450°C</td>
<td>&lt;250°C &lt;280°C</td>
<td>6.7x10^{-7}</td>
<td>0.6 &lt;0.8</td>
<td>20</td>
</tr>
<tr>
<td>Nano-Ag</td>
<td>&lt; 275°C</td>
<td>&lt; 961°C*</td>
<td>3.8</td>
<td>2.4</td>
<td>20 – 40</td>
</tr>
</tbody>
</table>
Nanosilver: developments needed

1. Adapt to thermoelectric materials
   **Difficulties:** Ionic conductivity of silver especially in chalcogenides

2. Less expensive alternatives
Objective 4. Metrology

4.1 TE material characterization exists
  \textit{OSU, NU, ZTPlus, BSST}

4.2 Electrical contact resistances
  \textit{ZTPlus}

4.3 Thermal contact resistances (new technique)
  \textit{Virginia Tech}

4.4 Device performance
  \textit{BSST}

4.5 Circular cross-check is now possible
  \Rightarrow \text{determination of the error bars}
4.1 Electrical contact resistances
4.2 Thermal contact measurements

Heating pulse power, $P$

$\tau$

Attached device

Thermal impedance: $Z_{th} = \frac{\Delta T}{P_H} = \frac{\Delta V}{K} = \frac{V_{F_i} - V_{F_f}}{I_H V_H (1-\phi) K}$

$V_{F_i}$: The initial VF value before application of heating power;
$V_{F_f}$: The final VF value after application of heating power;
$I_H$: The current applied to the DUT during the heating time in order to cause power dissipation;
$V_H$: The heating voltage resulting from the application of $I_H$ to the DUT;
$P_H$: The heating power pulse magnitude; product of $V_H$ and $I_H$;
$K$: Thermal calibration factor, in mV/°C;
Objective 5. Durability

1. Durability is built into every step of the design

1. Extensive durability testing at BSST and ZTPlus

BSST and ZTPlus, have state-of-the-art durability testing facilities used in the development of automotive products.

Ensure that this project incorporates automotive durability standards.
SUMMARY: FIVE objectives

1. New Materials
   1. Two systems: PbSe and Mg$_2$(Si, Sn)
   2. Two techniques: nanostructuring by liquid encapsulation, resonant levels

2. New thermal design: cross-flow heat and current

1. New Interface technologies
   1. Compliant highly conductive contacts, Ag nanopaste
   2. In-situ metallization during pellet consolidation
   3. Deposition techniques

• Metrology
  – New thermal contact resistance measurement technique
  – Self-consistency check: materials/interfaces/devices

• Reliability
  1. Design-inherent
  2. Automotive-level durability testing
Supplemental slides
1. Materials
   NU – OSU
   PbSe – based or Mg$_2$X (X=Ge, Si, Sn, Pb)

2. Thermal Management
   BSST
   Innovative Design and Architecture

3. Interfaces
   VT – ZTPlus
   New flexible Ag Nanopaste and metallization

4. Metrology
   BSST – OSU – NU
   VT – ZTPlus (ITE)
   Chemical and Physical characterization

5. Durability
   BSST – OSU – NU
   VT – ZTPlus
   Mechanical and Thermal shock resistance
PbSe-In and PbSe-Ga results: electrical conductivity

- Polycrystalline cast ingots
- Ga samples suffer from microcracks and other defects limiting mobility
- Both Ga and In efficiently generate carriers in PbSe
PbSe-Ga and PbSe-In: Seebeck

- Linear variation
- No saturation up to 900 K
- In doped samples have a higher thermopower at 700 K compared to Ga
- Reduced power factor ($S^2ne$) demonstrates the above
PbSe-Ga and PbSe-In: Reduced power factor 700K

Higher S yield for In samples for $1 \times 10^{19} < n < 5.5 \times 10^{19}$ cm$^{-3}$
PbSe-Ga and PbSe-In: Thermal conductivities

- Large room temperature values following large doping
- Total thermal conductivity stays above 1 W/mK
<table>
<thead>
<tr>
<th>Task</th>
<th>Description</th>
<th>Time Period in years</th>
<th>Years 1 – 3</th>
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<tbody>
<tr>
<td>1</td>
<td>Optimize thermoelectric properties of PbSe</td>
<td></td>
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<tr>
<td>1.1</td>
<td>Determine conditions for thermodynamic synthesis</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Develop bulk nanostructuring material by liquid encapsulation for Sb-PbSe, Bi-PbSe, Ga-PbSe, In-PbSe, As-PbSe</td>
<td>X</td>
<td>X</td>
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<tr>
<td>1.2.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
<td>X</td>
<td>X</td>
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<tr>
<td>1.2.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1.3</td>
<td>Introduce resonant impurities (In, Al, Ga, Tl)</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1.3.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
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<td></td>
</tr>
<tr>
<td>1.3.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1.4</td>
<td>Introduce 3d,4d or 5d elements and tune</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1.4.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
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<td>X</td>
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<tr>
<td>1.4.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
<td>X</td>
<td>X</td>
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<td></td>
<td><strong>Milestones</strong></td>
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</table>

*Project Phase*

*Task Description*

*Time Period in years*
## Optimize thermoelectric properties of $\text{Mg}_2\text{X}$ ($\text{Si,Sn,Pb}$)

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Completed</th>
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<tr>
<td>2.1</td>
<td>Determine conditions for thermodynamic synthesis</td>
<td>X</td>
</tr>
<tr>
<td>2.2</td>
<td>Develop bulk nanostructuring material by liquid encapsulation for $\text{Mg}<em>2\text{Si}</em>{1-x}\text{Sn}_x/\text{Y}$, $\text{Mg}<em>2\text{Si}</em>{1-x}\text{Pb}_x/\text{Y}$, $\text{Mg}<em>2\text{Sn}</em>{1-x}\text{Pb}_x/\text{Y}$ with $\text{Y} = \text{W,Mo, Ta, Hf, Nb}$</td>
<td>X</td>
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<td>2.2.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
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<tr>
<td>2.2.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
<td>X</td>
</tr>
<tr>
<td>2.3</td>
<td>Extend investigation with $\text{Y} = \text{stannides (Hf}_5\text{Sn}_3$, HfSn, La$_3$Sn$_5$, LaSn$_3$, CoSn, FeSn)</td>
<td>X</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
<td>X</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>Extend investigation with $\text{Y} = \text{silicides (Co}_2\text{Si, CoSi, CoSi}_2$, NiSi$_2$ (CaF$_2$ type), FeSi, LiAlSi, ZrSi$_2$, Zr$_2$Si, Zr$_3$Si, Hf$_2$Si, Hf$_3$Si$_2$, WSi$_2$, W$_5$Si$_3$, RuSi)</td>
<td>X</td>
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<tr>
<td>2.4.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
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<tr>
<td>2.4.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
<td>X</td>
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<tr>
<td>2.5</td>
<td>Introduce resonant level in $\text{Mg}<em>2\text{Pb}</em>{1-x}\text{X}_x$ $\text{X}=\text{Sb, Bi}$ for n-types</td>
<td>X</td>
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<tr>
<td>2.5.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
<td>X</td>
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<tr>
<td>2.5.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
<td>X</td>
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<tr>
<td>2.6</td>
<td>Introduce resonant level in $\text{Mg}<em>2\text{Pb}</em>{1-x}\text{X}_x$ $\text{X}=\text{Ga, In}$ for p-type or by substituting Mg by Na, Ag,</td>
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<tr>
<td>2.6.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
<td>X</td>
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<tr>
<td>2.6.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
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### Metallization of TE materials

<table>
<thead>
<tr>
<th>Milestones</th>
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<tbody>
<tr>
<td>3.1 For PbSe-based material (SPS)</td>
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</tr>
<tr>
<td>3.1.1 Develop blend of Fe/Sn or Pb chalcogenides</td>
<td>X</td>
</tr>
<tr>
<td>3.1.2 Chemical characterization of intermetallics (SEM/EDX)</td>
<td>X</td>
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<tr>
<td>3.1.3 Co-pressed the blend with PbSe by SPS</td>
<td>X</td>
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<tr>
<td>3.1.4 Chemical characterization of intermetallics (SEM/EDX)</td>
<td>X</td>
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<tr>
<td>3.1.5 Optimize densification properties</td>
<td>X</td>
</tr>
<tr>
<td>3.1.6 Measurement of the contact resistance</td>
<td>X</td>
</tr>
<tr>
<td>3.1.7 Durability test (thermal cycling and chock resistance)</td>
<td>X</td>
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<tr>
<td>3.1.8 Explore other barriers of diffusion co-pressed by SPS</td>
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</tr>
<tr>
<td>3.2 For PbSe-based material (PVD)</td>
<td>X</td>
</tr>
<tr>
<td>3.2.1 Identify potential element (e.g. nitride or carbide)</td>
<td>X</td>
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<tr>
<td>3.2.2 Development of the sputtering process</td>
<td>X</td>
</tr>
<tr>
<td>3.2.3 Chemical characterization (SEM/EDX)</td>
<td>X</td>
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<tr>
<td>3.2.4 Measurement of the contact resistance</td>
<td>X</td>
</tr>
<tr>
<td>3.2.5 Durability test (thermal cycling and chock resistance)</td>
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</tbody>
</table>
## Metallization of TE materials

### 3.3 Develop a process for Mg₂X (SPS)
- Identify potential blend
- Co-pressed the blend with Mg₂X by SPS
- Chemical characterization of intermetallics (SEM/EDX)
- Optimize densification properties
- Measurement of the contact resistance
- Durability test (thermal cycling and chock resistance)

### 3.4 Develop a process for Mg₂X (PVD)
- Identify potential element (e.g. nitride or carbide)
- Development of the sputtering process
- Chemical characterization (SEM/EDX)
- Measurement of the contact resistance
- Durability test (thermal cycling and chock resistance)

### Milestones

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<tr>
<th>Step</th>
<th>Task</th>
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<tr>
<td>3.3</td>
<td>Develop a process for Mg₂X (SPS)</td>
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<td>3.3.1</td>
<td>Identify potential blend</td>
<td>X X</td>
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<tr>
<td>3.3.2</td>
<td>Co-pressed the blend with Mg₂X by SPS</td>
<td>X X</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Chemical characterization of intermetallics (SEM/EDX)</td>
<td>X X</td>
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<tr>
<td>3.3.4</td>
<td>Optimize densification properties</td>
<td>X X</td>
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<tr>
<td>3.3.5</td>
<td>Measurement of the contact resistance</td>
<td>X</td>
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<tr>
<td>3.3.6</td>
<td>Durability test (thermal cycling and chock resistance)</td>
<td>X X</td>
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<tr>
<td>3.4</td>
<td>Develop a process for Mg₂X (PVD)</td>
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</tr>
<tr>
<td>3.4.2</td>
<td>Development of the sputtering process</td>
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<tr>
<td>3.4.3</td>
<td>Chemical characterization (SEM/EDX)</td>
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<tr>
<td>3.4.4</td>
<td>Measurement of the contact resistance</td>
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<tr>
<td>3.4.5</td>
<td>Durability test (thermal cycling and chock resistance)</td>
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# Milestones

<table>
<thead>
<tr>
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<th>Device interconnection (bonding element to heat spreader)</th>
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<tr>
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<tr>
<td>4.1</td>
<td>Chemical investigation of Ag diffusion in metallization (SEM/XPS)</td>
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<td>4.1.1</td>
<td>Influence of the amount of Ag</td>
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<tr>
<td>4.1.2</td>
<td>Influence of coating gold on Ag joint</td>
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<tr>
<td>4.1.3</td>
<td>Measurement of the contact resistance</td>
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<tr>
<td>4.2</td>
<td>Study of other metals (M)</td>
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<tr>
<td>4.2.1</td>
<td>Chemical investigation of M diffusion in metallization (SEM/XPS)</td>
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<td>4.2.2</td>
<td>Influence of the amount of M</td>
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<tr>
<td>4.2.3</td>
<td>Measurement of the contact resistance</td>
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## Milestones

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<th>Integration of material and interfaces into patented module</th>
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<tr>
<td>5.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
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<td>5.2</td>
<td>Measurement of the contact resistance</td>
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<tr>
<td>5.3</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
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<tr>
<td>5.4</td>
<td>Durability test</td>
<td></td>
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</tbody>
</table>

### 6 Develop new module/heat exchanger design

<table>
<thead>
<tr>
<th></th>
<th>Develop new module/heat exchanger design</th>
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</thead>
<tbody>
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<tr>
<td>6.1</td>
<td>Chemical characterization (XRD/SEM/EDX)</td>
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<tr>
<td>6.2</td>
<td>Thermoelectric characterization: measuring, analyzing</td>
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<tr>
<td>6.3</td>
<td>Measurement of the contact resistance</td>
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<tr>
<td>6.4</td>
<td>Durability test</td>
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