DOE/NSF Thermoelectric Partnership
Project SEEBECK

Saving **E**nergy **E**ffectively **B**y **E**ngaging in **C**ollaborative research and sharing **K**nowledge

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2012 DOE Annual Merit Review, Crystal City Marriott, 18 May 2012
Report up to 16 March 2012

Project ID#: ACE068

Overview

Timeline

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

Budget

Total (NSF+DOE): $1,453,532
DOE share: 50% (unverified)

- Funding FY11: $478,907

OSU+subcontracts: $240,411
NU: $126,403
VT: $112,093

- Funding FY12:

OSU+subcontracts: $204,135
NU: $127,711
VT: $114,413

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

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:
   - 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
   - Electrical and Thermal interface resistance measurements
   - Overall system performance measurements
   - Internal check: all of the above are redundant
5. Durability:
   - Compatible with automotive durability requirements

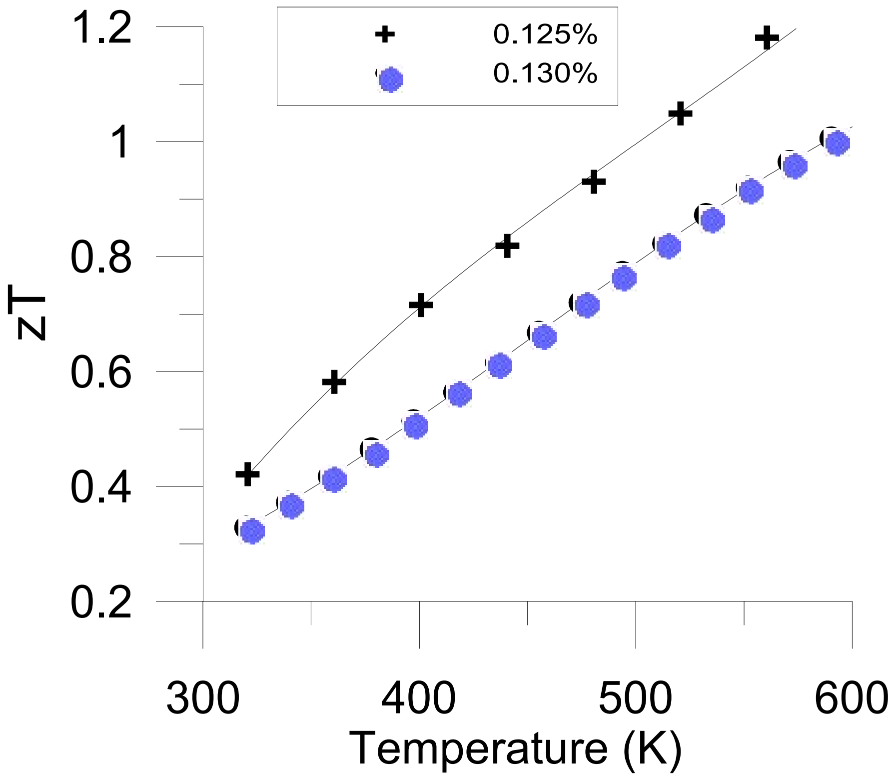
Approach 1: PbSe Figure of Merit, Intermediate-T

Last year: ZT ~ 0.9 at 750 K

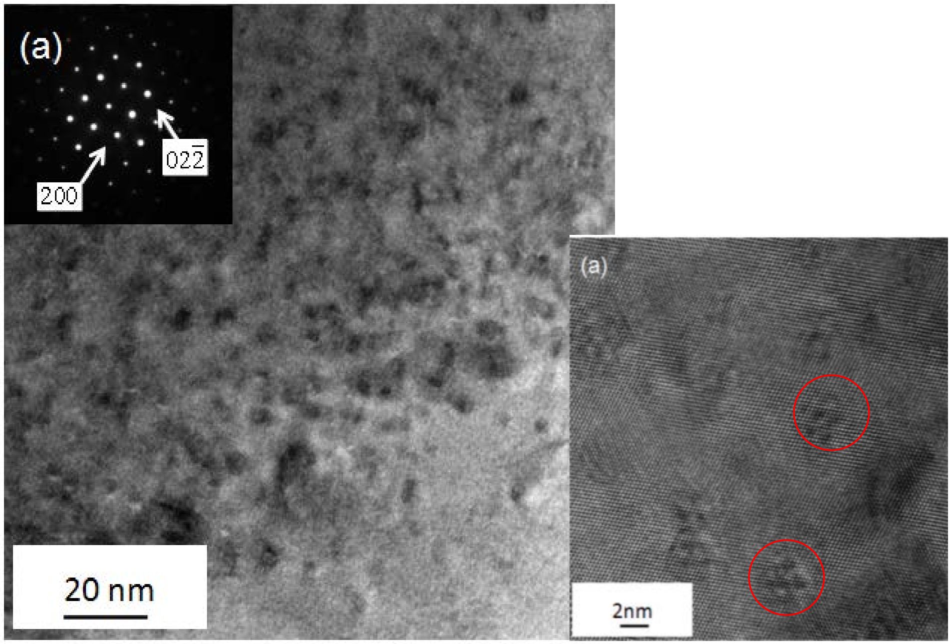
Waste-heat recovery systems cannot use the full exhaust-gas T-range:

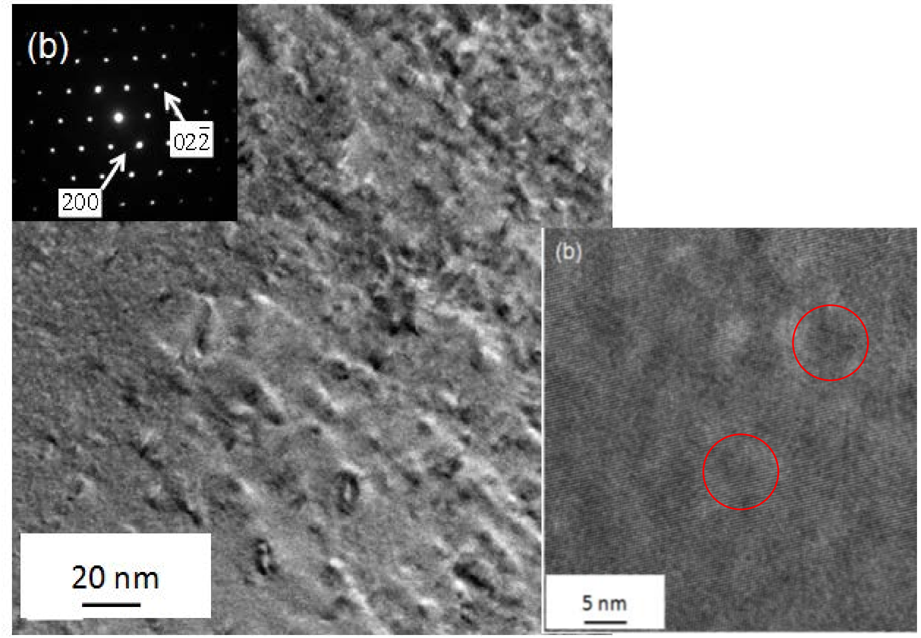
- Account for heat losses at interfaces
- Account for engine operating regimes

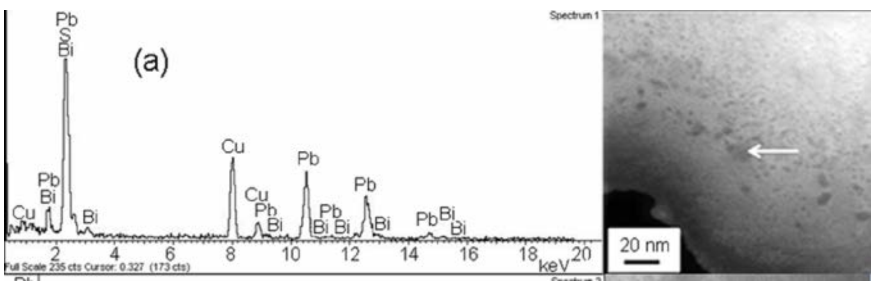
In-doped PbSe **ZT reaches 1.2 at 580 K** (Joint NU/OSU work).

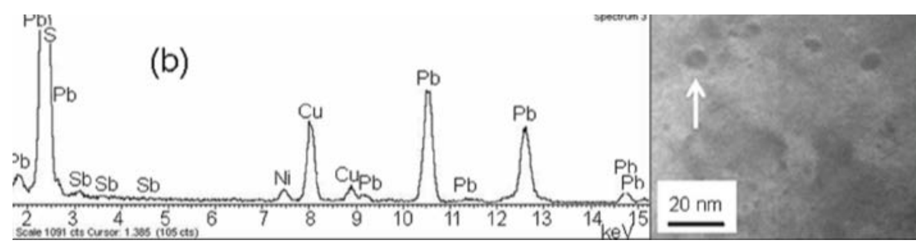


Approach 1: PbS doped with Cl
Liquid encapsulation reduces thermal conductivity (NU)

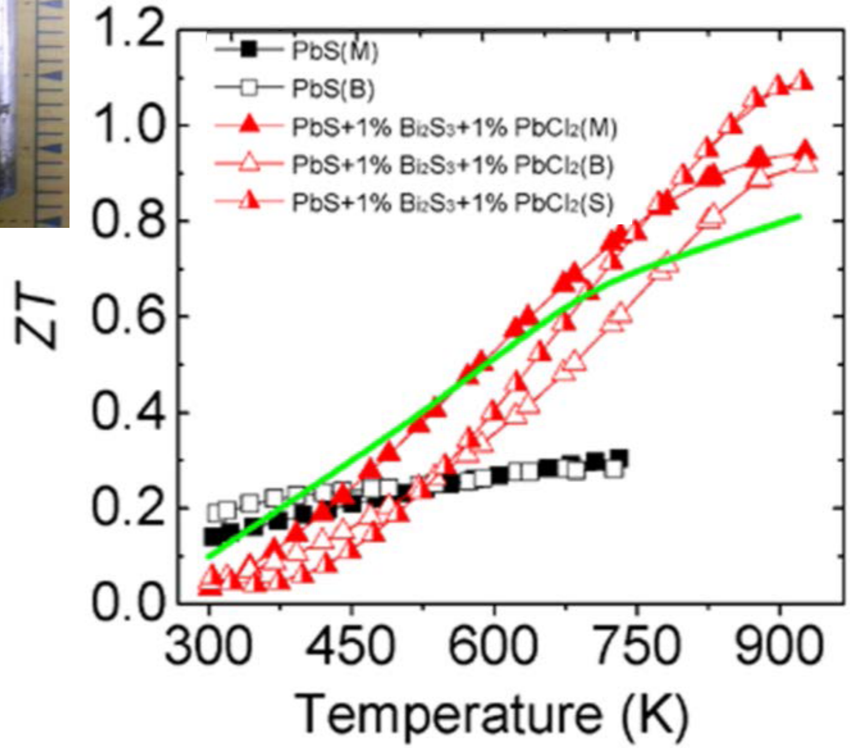


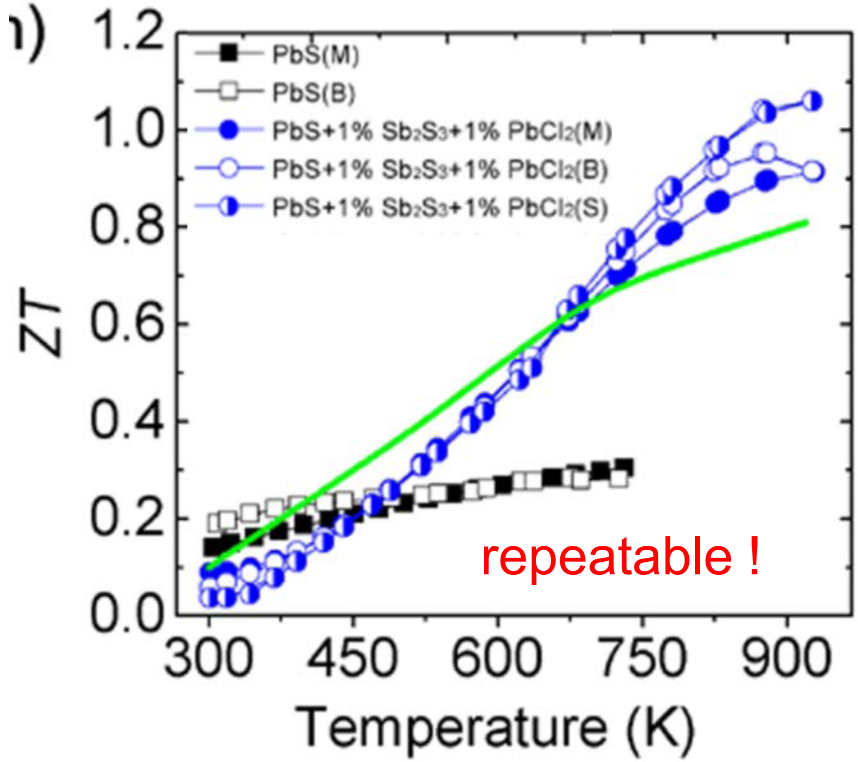






Approach 1: PbS doped with Cl
ZT>1 in materials less expensive per weight than Mg_2Si





Future: PbS very promising
Develop P-type material
Further increase ZT: resonant levels, nanostructuring

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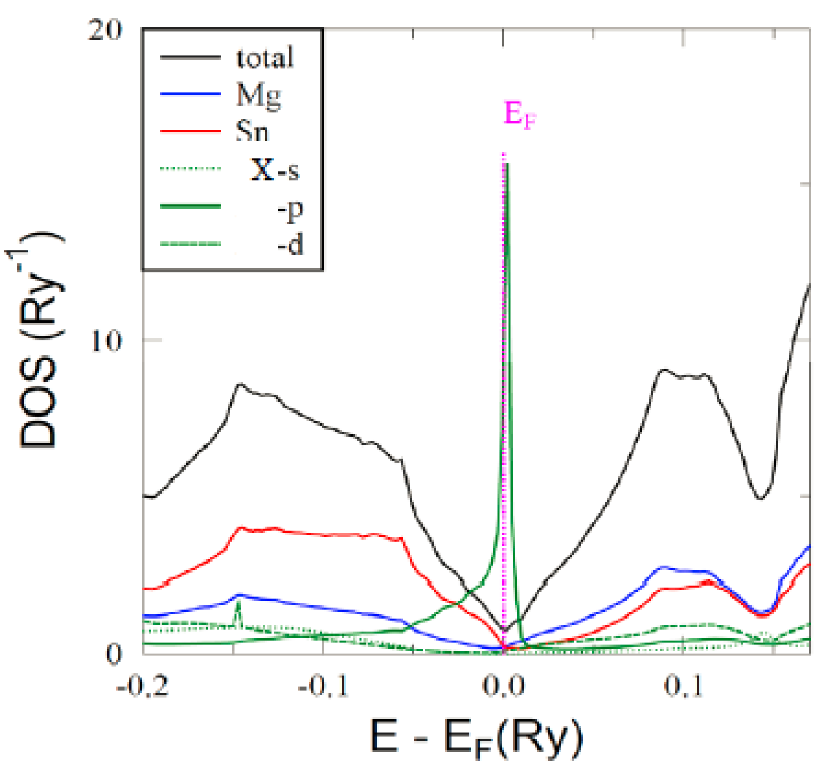
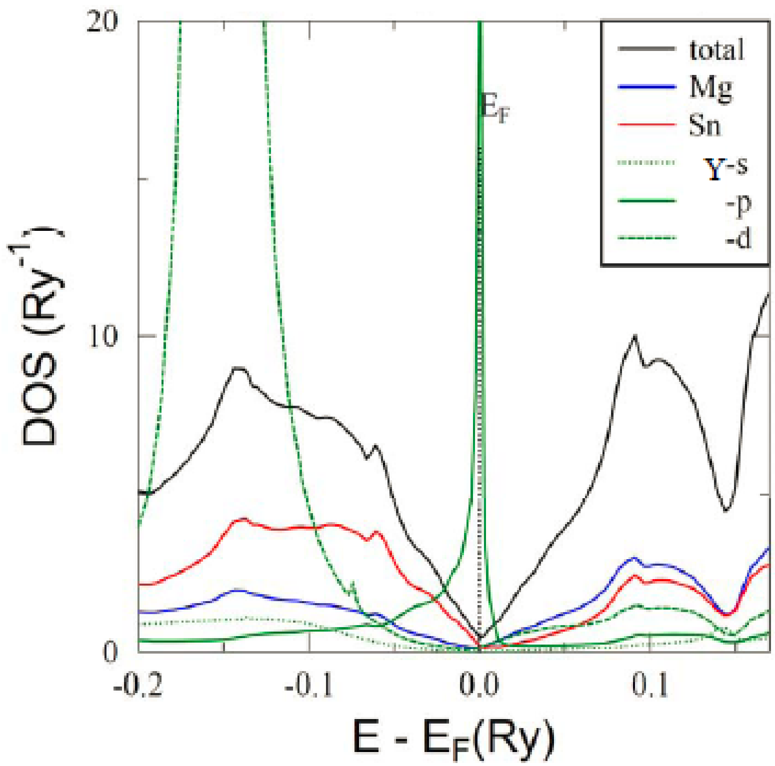
Approach 2: Resonant levels in Mg_2Sn

- **Candidate dopants identified** by band structure calculations (J. Tobola)
- Select from list of candidates





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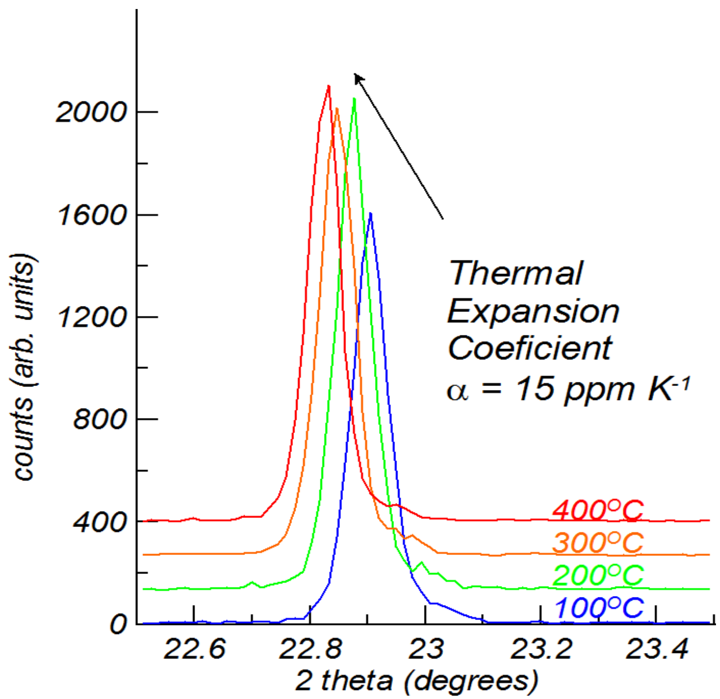
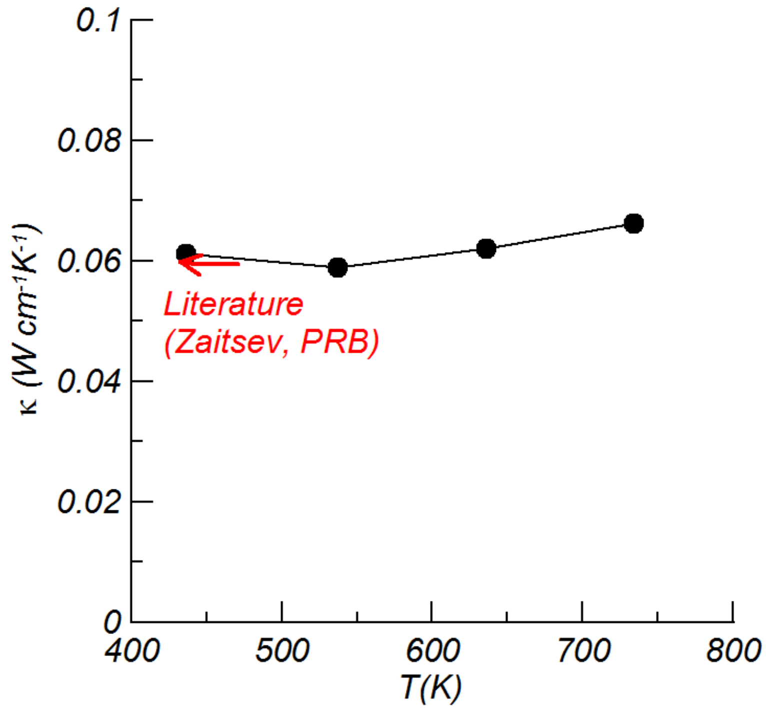
Approach 2: First data on Mg_2Sn

- **Synthesis successful**
- X-ray characterization: large thermal expansion coefficient
- Expect large anharmonicity, low lattice thermal conductivity





Future: 1. Mg_2Sn,Si at both OSU and NU
2. Need to perfect stoichiometry control
3. Dope with resonant levels

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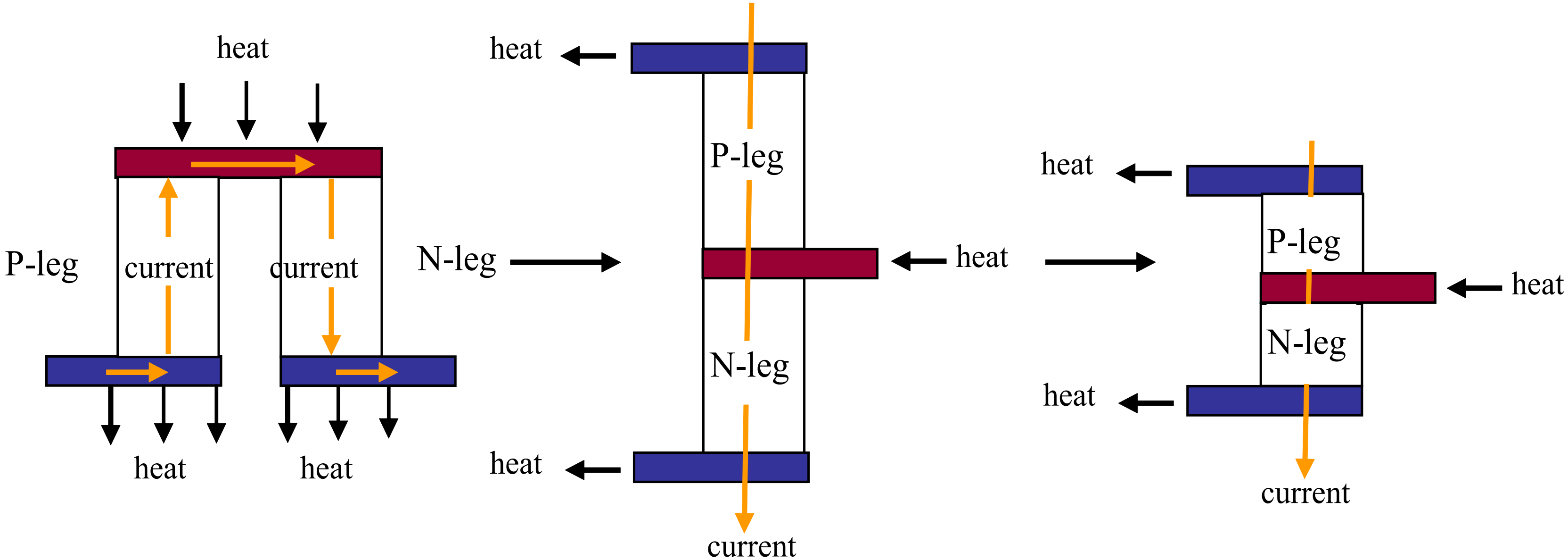
Objective 2.
New designs for thermal management



1. Reduced number of interfaces and components => reduced losses
2. High power density materials => much smaller sizes
3. Segmentation across the temperature differential => max. efficiency

Achievements:

1. Design currently in use at BSST
2. Need new materials & metallization to adapt it to

Future: Material transfer from (OSU,NU) => VT => ZTPlus
Incorporate materials & contacts developed under objectives 1 & 3

Objective 3. Interfaces

Compliant, high electrical and thermal conductance

New compliant thermoelectric device interconnects using nanosilver

Problem addressed: interdiffusion between chalcogen atoms in thermoelectric material and silver in contacts

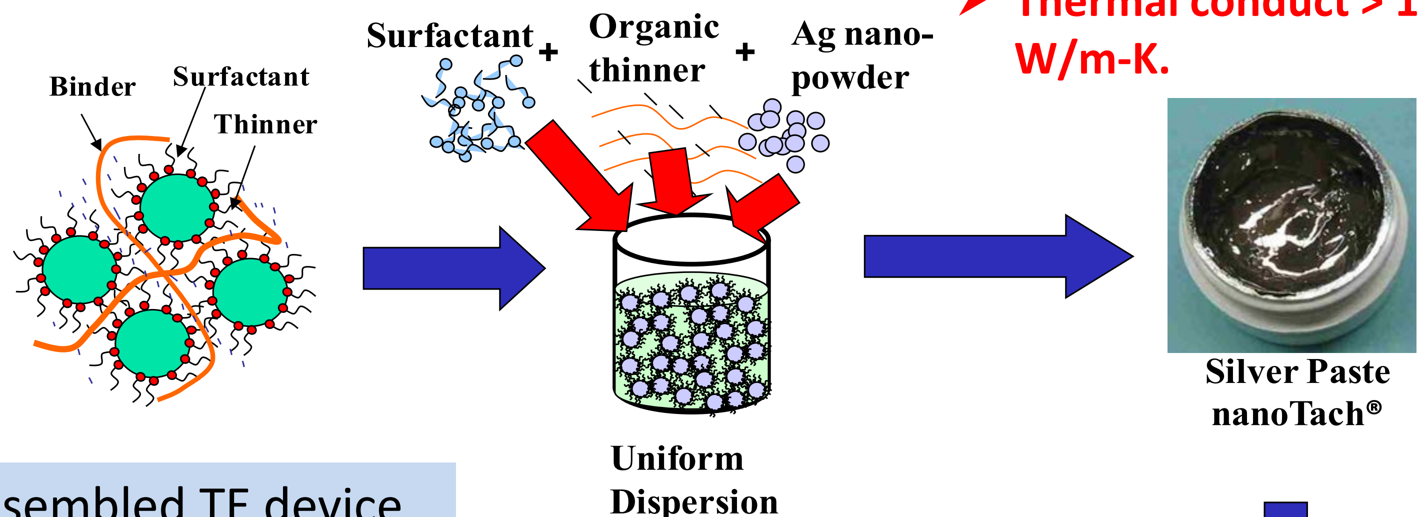
Achievement this year: **development of a diffusion barrier**

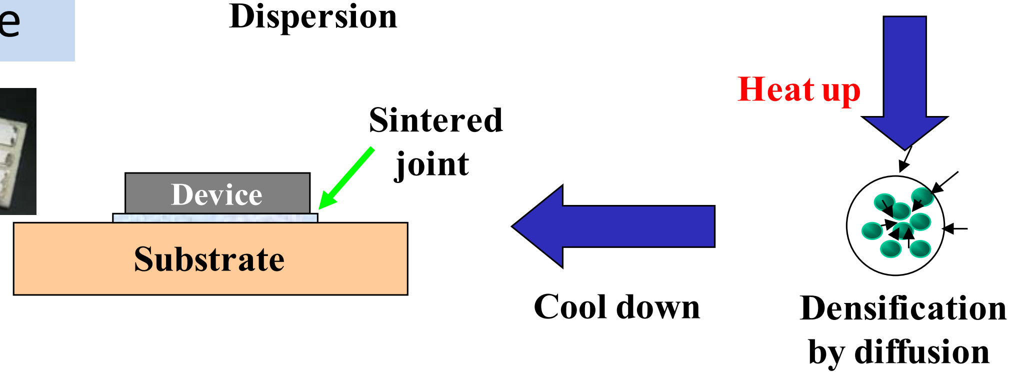
Future:
Incorporate this result in materials developed under Objective 1
Materials transfer from (OSU, NU) => VT

Approach:
Nanosilver interconnect packaging material

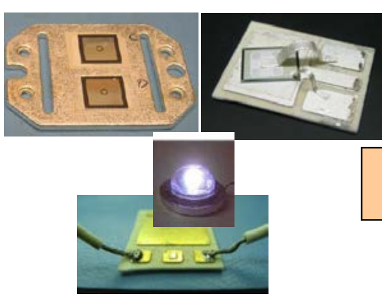
Pb-free, high-T die-attach solution:

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





Assembled TE device

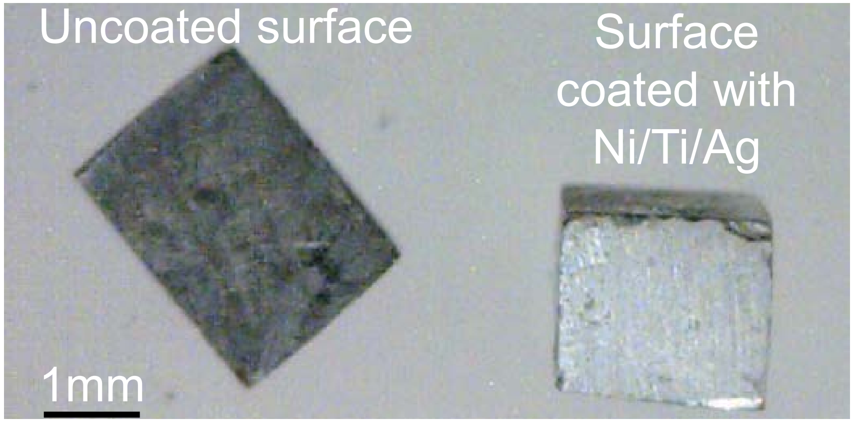


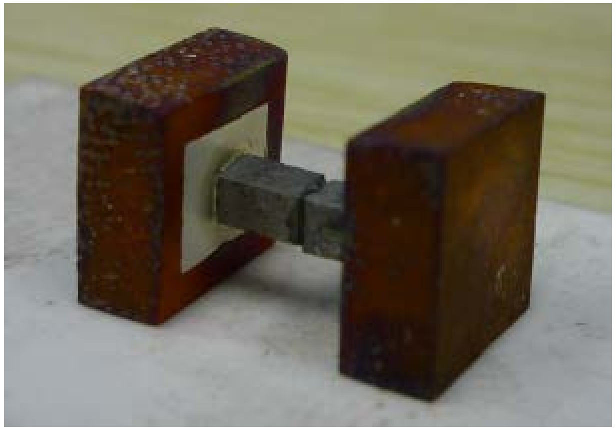
Approach:
Join thermoelectric couples by nanosilver sintering

1. TE material from OSU Partner

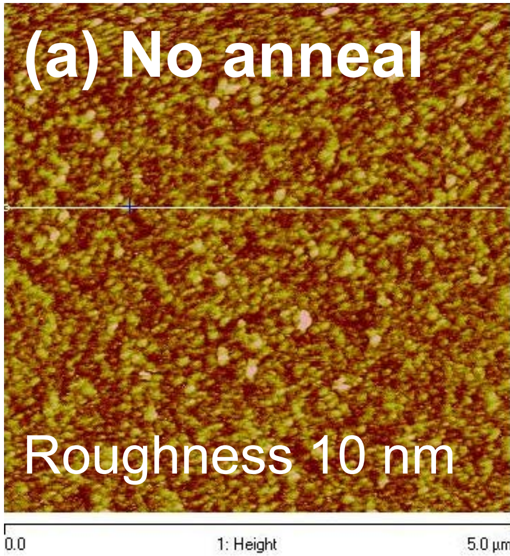
2. Processing steps:

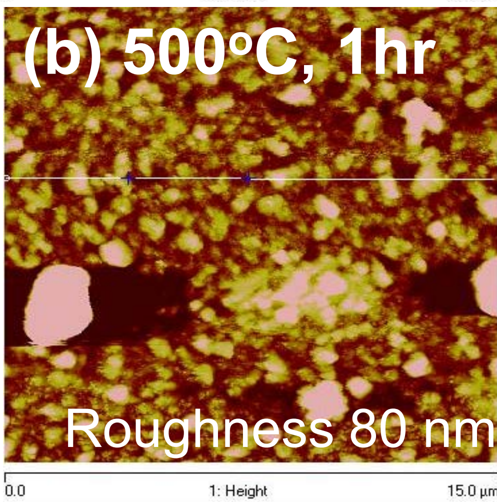
- Coat TE elements with Ni, Ti, and Ag respectively (100 nm for each layer);
- Print nanosilver paste on the ends of TE elements and Cu substrates;
- Assemble the structure and go through the drying and sintering process.



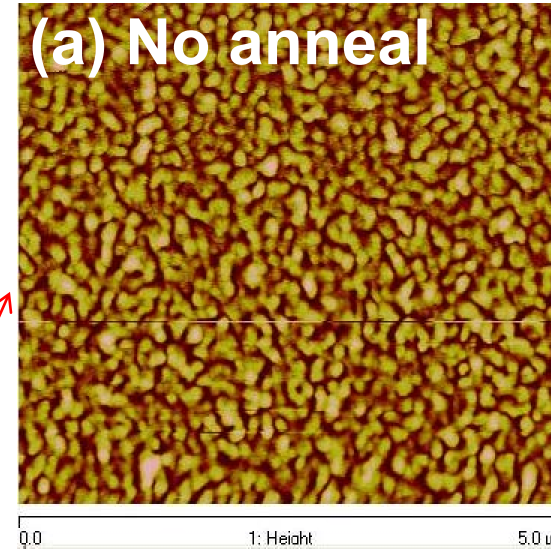


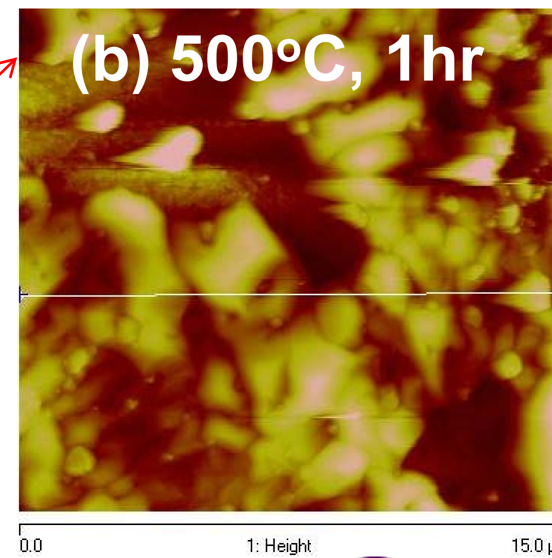
Approach: Diffusion barrier layers to silver





Titanium alone:
Diffusivity Ag/Ti = $2\times10^{-15}cm^2/s$





Ti-W bilayer:
Diffusivity Ag << 1×10^{-15} cm^2/s

- No increase of Ag was found in the sample
- **Ti-W blocks Ag diffusion**

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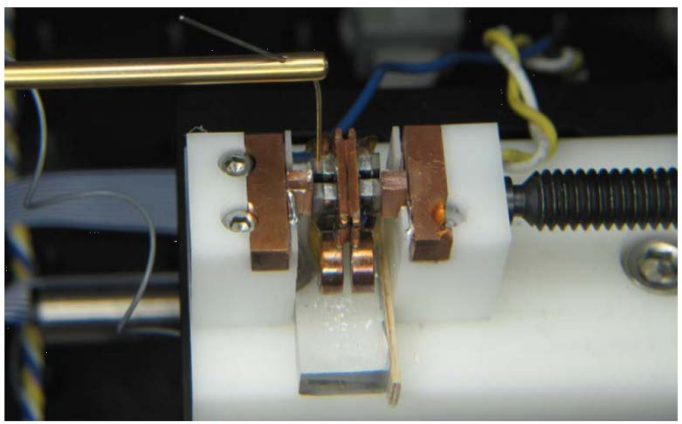
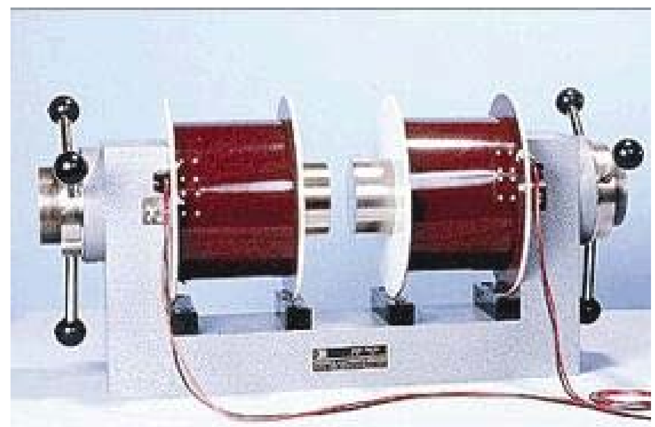
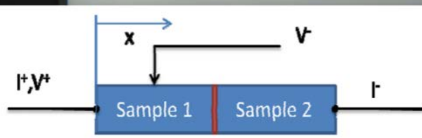
Objective 4: Metrology

4.1 TE material characterization exists
4.2 Electrical contact resistances: ZTPlus
4.3 Thermal contact resistances (new technique): Virginia Tech
4.4 Device performance: BSST
4.5 Circular cross-check will be possible => determination of the error bars

Achievements this year: **contact resistance metrology in place (ZT Plus)**







Future:
Apply this to contacts developed under objective 3
Materials transfer from VT => ZTPlus

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Objective 5. Durability
Ensure that this project incorporates automotive durability standards.

1. Durability is built into every step of the design
2. 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.

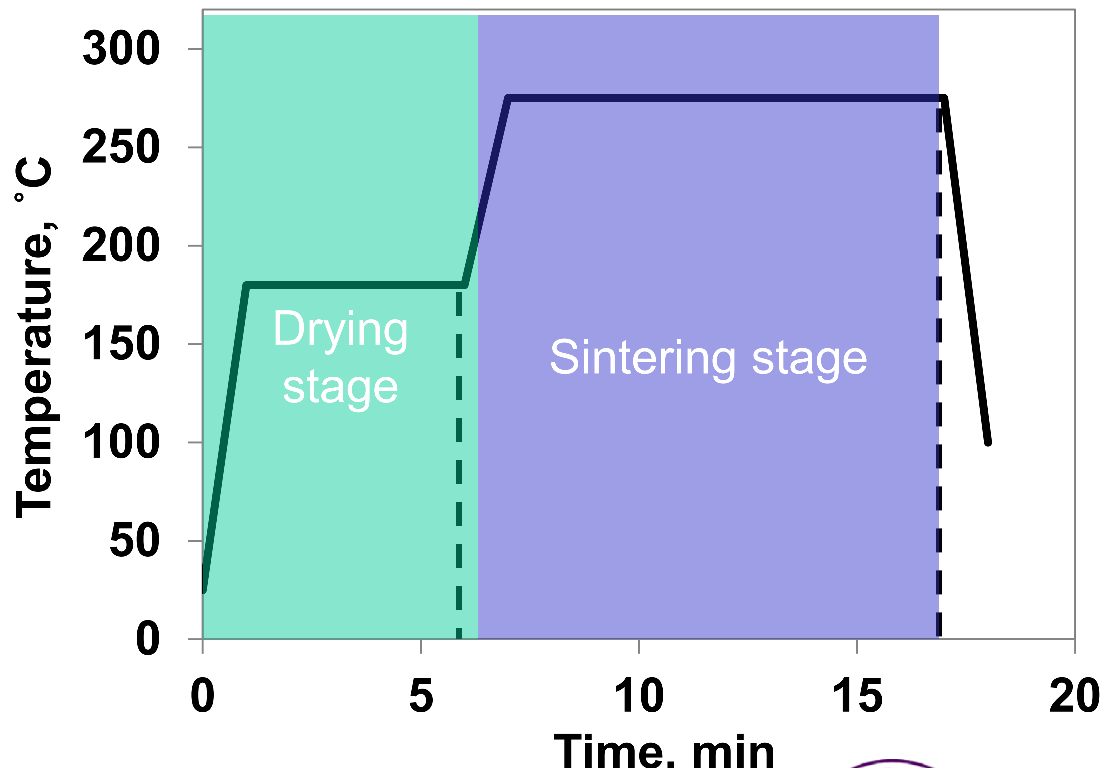
Achievement this year:
Nanosilver TE-material die attach shear strength

Future:
Apply to materials and contacts developed under Objectives 1 & 3
Materials transfer (OUSU+NU) => VT => ZTPlus => BSST

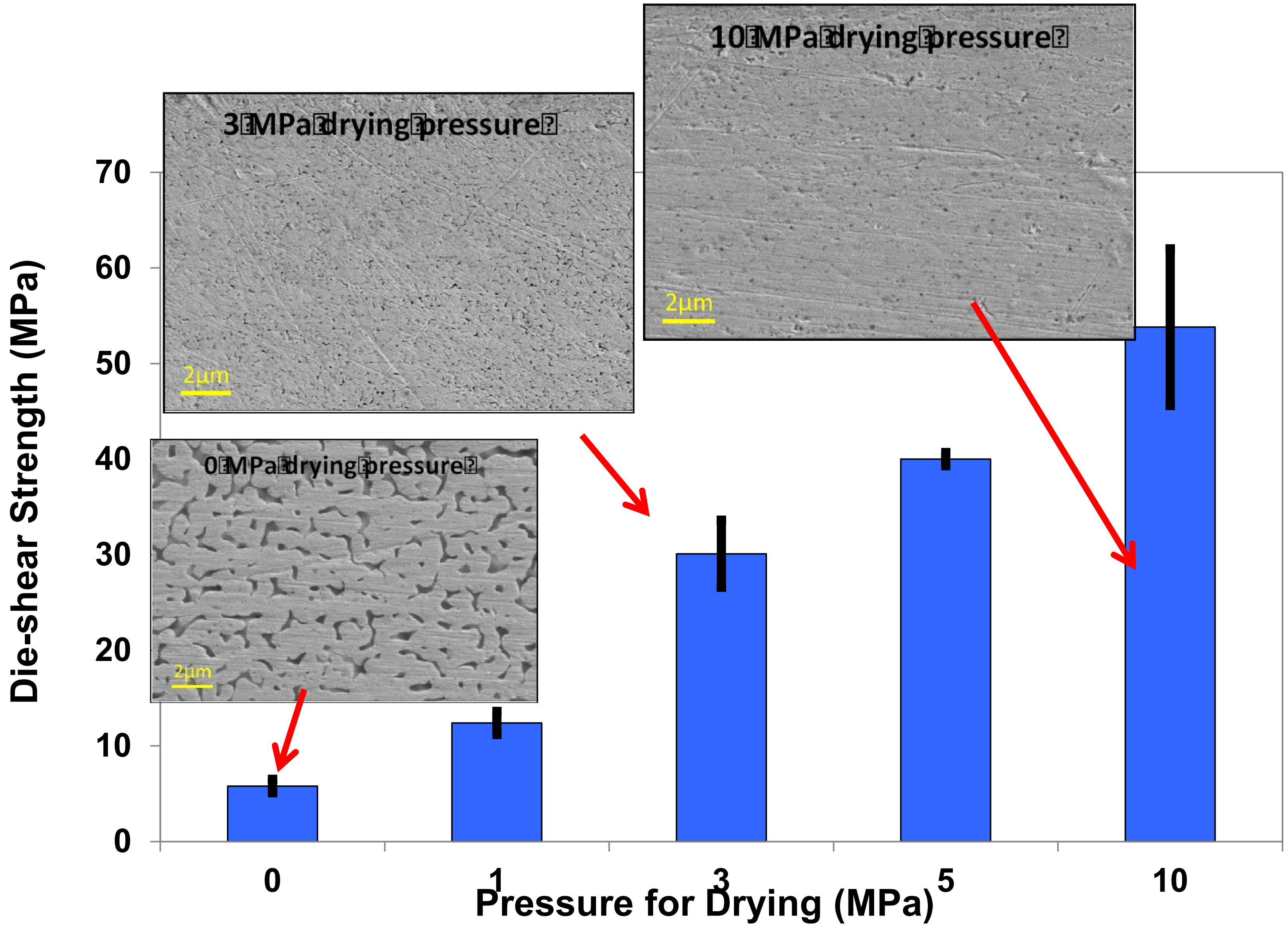
Approach
Optimize pressure at drying stage on TE die bond quality

Process:

- Print a layer of nanosilver paste on substrate with thickness of 50 μm;
- drying the print at 180°C for 5 minutes by heating from room temperature (5°C/min);
- applying a second layer of the paste on the dried print to a thickness of 10μm;
- Mount a device on fresh print;
- dry at 180 C for 5min under 0 - 10 MPa;
- sinter at 275 C for 10 min without pressure.



Approach
Pressure at drying stage Optimized: TE die bond quality



SUMMARY: FIVE objectives

1. New Materials
   1. PbSe Record ZT's achieved; Expand to cheaper PbS
   2. $Mg_2(Si, Sn)$: Synthesis on target; Identified RLs; start doping
2. New thermal design:
   1. Exists; Will incorporate new materials
3. New Interface technologies: flexible Ag nanopaste
   1. Address interdiffusion problem, developed diffusion barrier layer
4. Metrology:
   1. In place
   2. On standby, awaiting availability of new materials/bonds (as per plan)
5. Reliability: inherent in design
   1. Optimized mounting shear strength

Future work plans: explained for each objective

Collaboration is inherent, flow of materials from partner to partner.

Technical back-up slides

Milestones (bold = achieved, ← = pulled forward)

Summary: record ZT's achieved after year 1 => expand to cheaper alternative PbS

Project Phase		Years 1 – 3		
Task	**Description** *Time Period in years*	**1**	**2**	**3**
1	**Optimize thermoelectric properties of PbSe**			
1.1	Determine conditions for thermodynamic synthesis	**X**		
1.2	Develop bulk nanostructuring material by liquid encapsulation for Sb-PbSe, Bi-PbSe, Ga-PbSe, In-PbSe, As-PbSe	**X**	X	X
1.2.1	Chemical characterization (XRD/SEM/EDX)	**X**	X	X
1.2.2	Thermoelectric characterization: measuring, analyzing	**X**	X	
1.3	Introduce resonant impurities (In, Al, Ga, Tl)	**X**	X	X
1.3.1	Chemical characterization (XRD/SEM/EDX)	**X**		
1.3.2	Thermoelectric characterization: measuring, analyzing	←	X	X
1.4	Introduce 3d,4d or 5d elements and tune	←	X	X
1.4.1	Chemical characterization (XRD/SEM/EDX)	←	X	X
1.4.2	Thermoelectric characterization: measuring, analyzing	←	X	X

2	**Optimize thermoelectric properties of Mg_2X (Si,Sn,Pb)**			
2.1	Determine conditions for thermodynamic synthesis	**X**		
2.2	Develop bulk nanostructuring material by liquid encapsulation for $Mg_2Si_{1-x}Sn_x/Y$, $Mg_2Si_{1-x}Pb_x/Y$, $Mg_2Sn_{1-x}Pb_x/Y$ with Y= W,Mo, Ta, Hf, Nb	**X**	X	X
2.2.1	Chemical characterization (XRD/SEM/EDX)	←	X	X
2.2.2	Thermoelectric characterization: measuring, analyzing	←	X	X
2.3	Extend investigation with Y = stannides (Hf_5Sn_3, HfSn, La_3Sn_5, $LaSn_3$, CoSn, FeSn)			X
2.3.1	Chemical characterization (XRD/SEM/EDX)			X
2.3.2	Thermoelectric characterization: measuring, analyzing			
2.4	Extend investigation with Y = silicides (Co_2Si, CoSi, $CoSi_2$, $NiSi_2$ (CaF_2 type), FeSi, LiAlSi, $ZrSi_2$, Zr_2Si, Zr_3Si, Hf_2Si, Hf_3Si_2, WSi_2, W_5Si_3, RuSi)			X
2.4.1	Chemical characterization (XRD/SEM/EDX)			X
2.4.2	Thermoelectric characterization: measuring, analyzing			X
2.5	Introduce resonant level in $Mg_2Pb_{1-x}X_x$ X=Sb, Bi for n-types	**X**	X	
2.5.1	Chemical characterization (XRD/SEM/EDX)		X	
2.5.2	Thermoelectric characterization: measuring, analyzing		X	X
2.6	Introduce resonant level in $Mg_2Pb_{1-x}X_x$ X=Ga, In for p-type or by substituting Mg by Na, Ag,		X	X
2.6.1	Chemical characterization (XRD/SEM/EDX)		X	X
2.6.2	Thermoelectric characterization: measuring, analyzing		X	X

Milestones (bold = achieved, ← = pulled forward)

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

Milestones

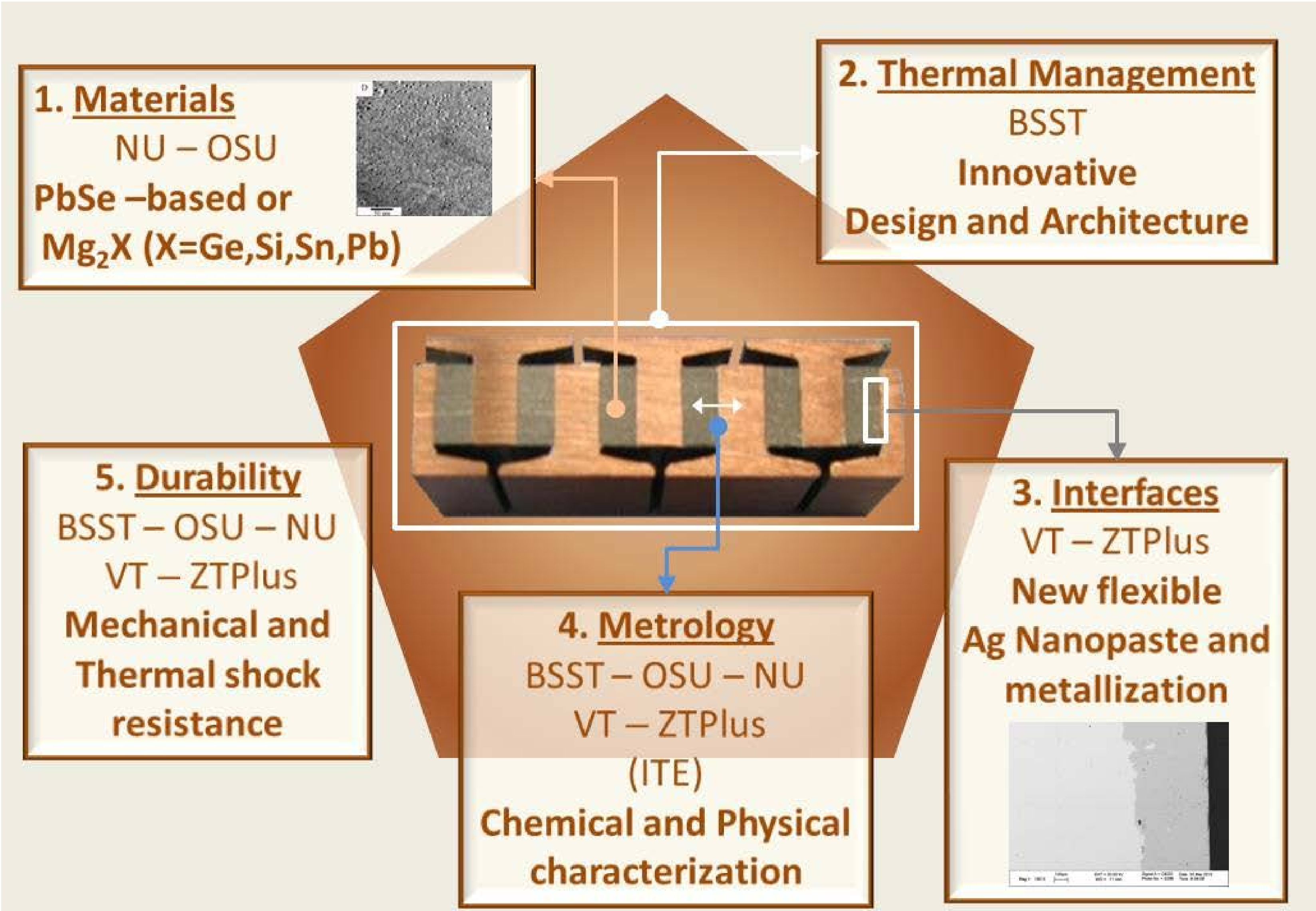
3	**Metallization of TE materials**			
3.3	Develop a process for Mg_2X (SPS)		X	X
3.3.1	Identify potential blend		X	X
3.3.2	Co-pressed the blend with Mg_2X by SPS		X	X
3.3.3	Chemical characterization of intermetallics (SEM/EDX)		X	X
3.3.4	Optimize densification properties		X	X
3.3.5	Measurement of the contact resistance			X
3.3.6	Durability test (thermal cycling and chock resistance)		X	X
3.4	Develop a process for Mg_2X (PVD)		X	
3.4.1	Identify potential element (e.g. nitride or carbide)		X	X
3.4.2	Development of the sputtering process		X	
3.4.3	Chemical characterization (SEM/EDX)		X	
3.4.4	Measurement of the contact resistance			X
3.4.5	Durability test (thermal cycling and chock resistance)			X

Milestones (bold = achieved, ← = pulled forward)

4	**Device interconnection (bonding element to heat spreader)**			
4.1	Chemical investigation of Ag diffusion in metallization (SEM/XPS)	**X**		
4.1.1	Influence of the amount of Ag	**X**		
4.1.2	Influence of coating gold on Ag joint	X	X	
4.1.3	Measurement of the contact resistance	X	X	
4.2	Study of other metals (M)	←		X
4.2.1	Chemical investigation of M diffusion in metallization (SEM/XPS)	←		X
4.2.2	Influence of the amount of M	←		X
4.2.3	Measurement of the contact resistance	X	X	X

Milestones (bold = achieved, ← = pulled forward)

5	**Integration of material and interfaces into patented module**			
5.1	Chemical characterization (XRD/SEM/EDX)		X	
5.2	Measurement of the contact resistance		X	X
5.3	Thermoelectric characterization: measuring, analyzing			x
5.4	Durability test	**x**	x	x
6	**Develop new module/heat exchanger design**			
6.1	Chemical characterization (XRD/SEM/EDX)		X	
6.2	Thermoelectric characterization: measuring, analyzing		X	X
6.3	Measurement of the contact resistance		X	X
6.4	Durability test		X	X



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