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

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Presentation
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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 ehaust 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 measuremenst
   - 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

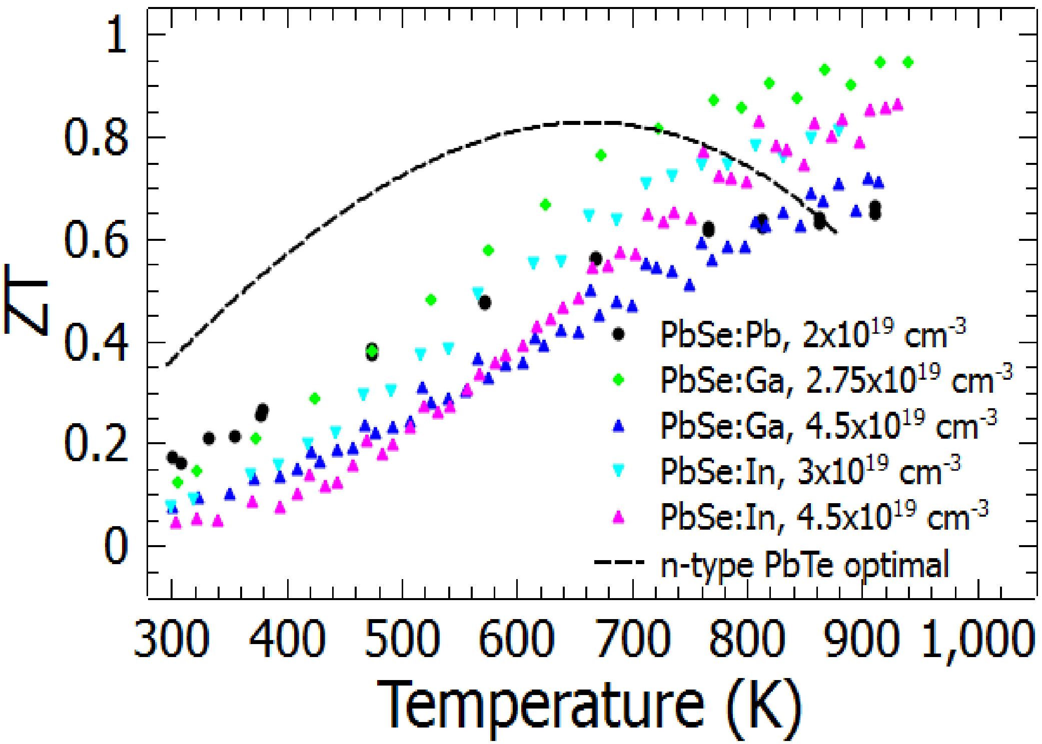
1. Accomplishement: theoretical study identifies In level in PbSe

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

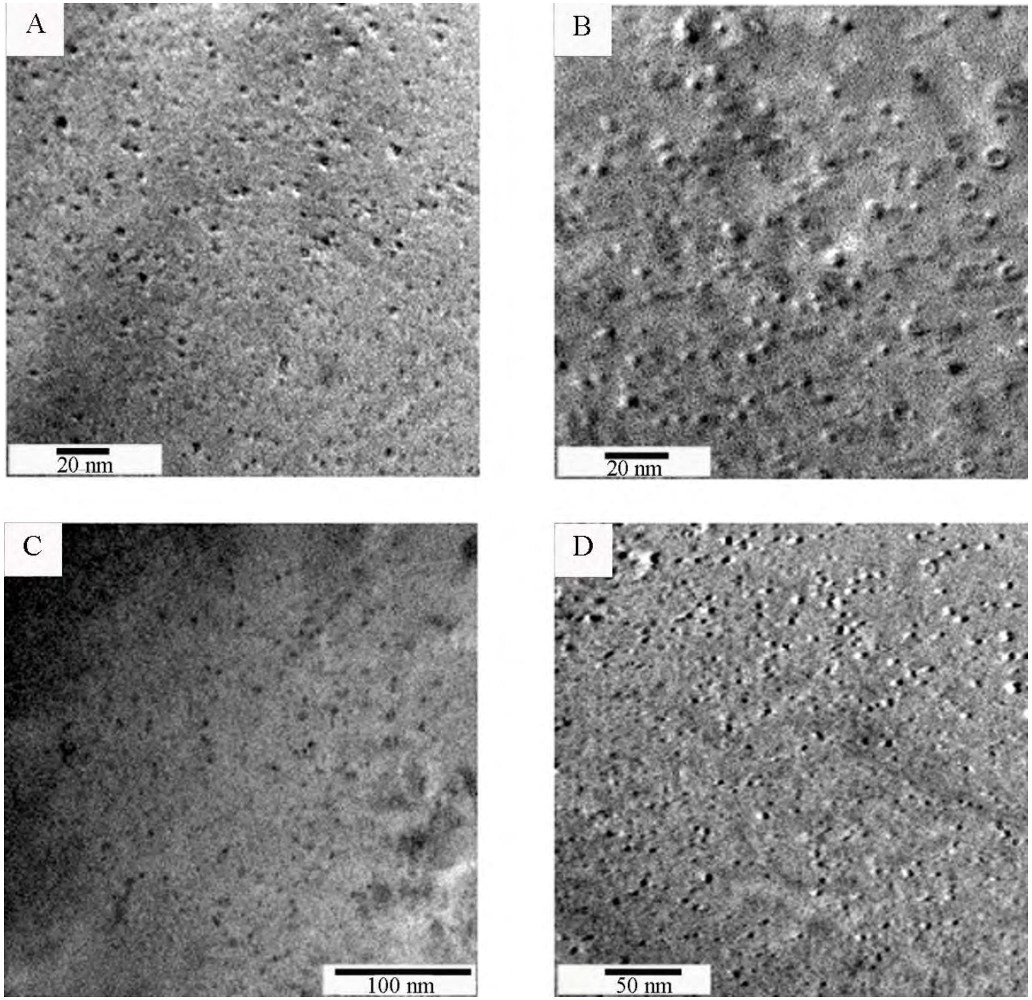


ZT reaches 0.9 at 900 K.

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%).

Objective 1.2.1 Resonant levels in $Mg_2(Si,Sn)$

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. Accomplishement: Shubnikov-de Haas measurements on single-crystal Mg_2 Sn doped with Ag

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

m_c (.25% Ag) = 0.013, 0.025 m_e
m_c (1% Ag) = 0.005, 0.011 m_e
Same result for <111> <220>

Objective 1.2.2 Nanostructuring Mg_2(Si,Sn)

Concept: use liquid encapsulation

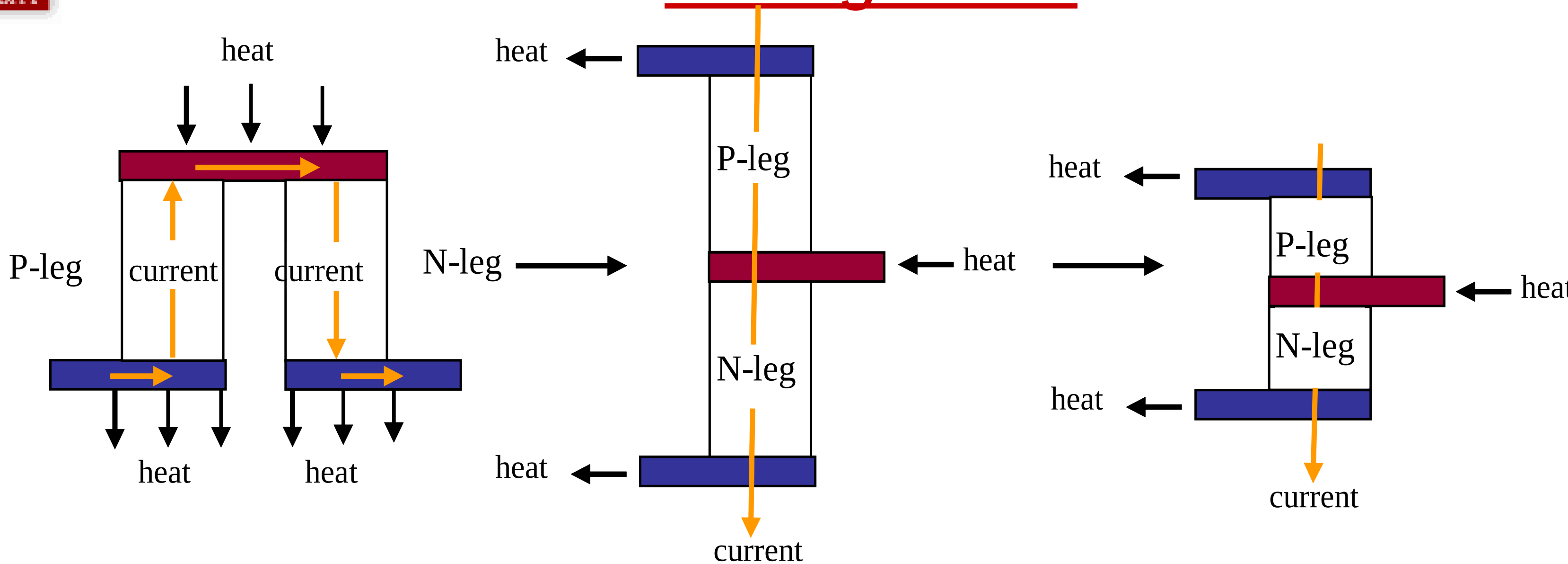
$Mg_2Si_{1-x}Sn_x$/Y, $Mg_2Si_{1-x}Pb_x$/Y and $Mg_2Sn_{1-x}Pb_x$/Y systems that melt congruently

Y as element

Y as compound that do not form compounds with Mg_2X :

- binary silicides Co_2Si, ...
- binary stannides: Hf_5Sn_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.

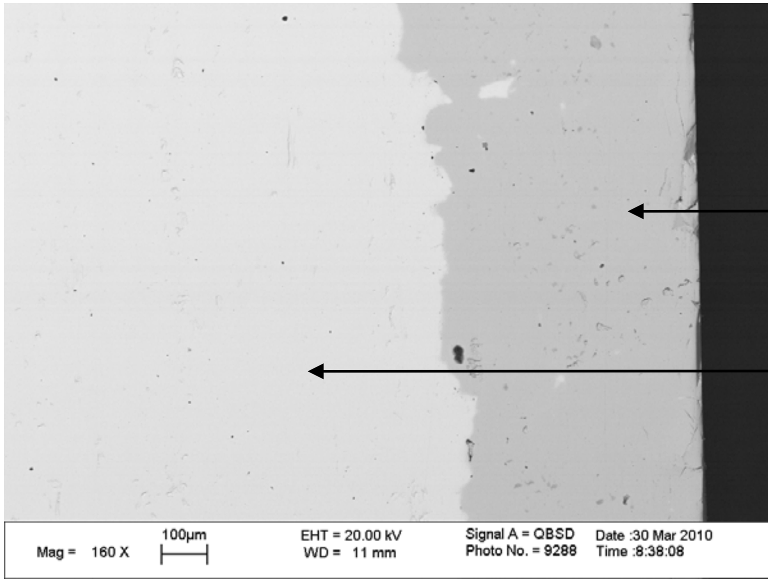
3.2 New compliant device interconnects

3.2.1 Nanosilver

3.2.2 New systems

Objective 3.1 TE material metallization

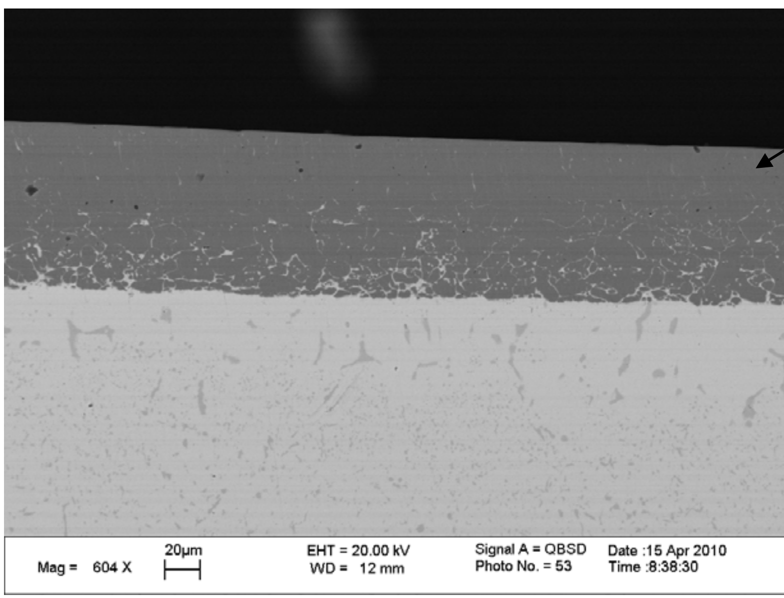
Direct co-sintering during material consolidation (SPS)



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

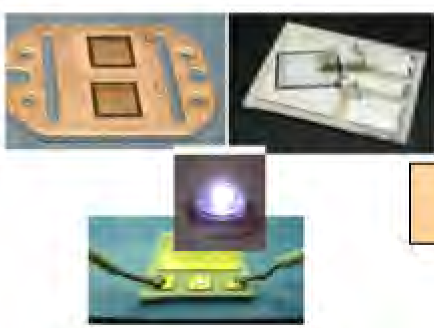
Issues: interdiffusion, diffusion barriers

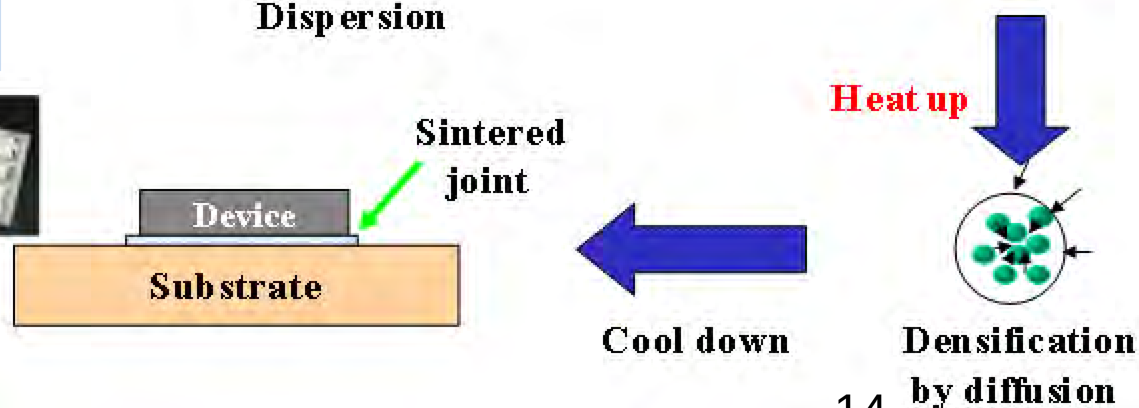
Objective 3.2 Nanosilver interconnect packaging material

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

	Processing temperature	Max. use temperature	Electrical conductivity $10^5\ (\Omega\text{-cm})^{-1}$	Thermal conductivity (W/K-cm)	Die-shear Strength (MPa)
Lead-tin solder	217ºC	< 183ºC	0.69	0.51	35
Lead-free solder	260ºC	< 225ºC	0.75	0.70	35
Gold-tin solder	310ºC	< 280ºC	0.625	0.58	30 - 60
Silver epoxy	100 – 200ºC	< 200ºC	0.1	0.1	10 – 40
High-Pb solder	340ºC	< 280ºC	0.45	0.23	15
Hysol® QMI 3555 R	300 – 450ºC	<250[illegible] <280ºC	6.7x10-7	0.[illegible] <0.8	20
Nano-Ag	< 275ºC	< 961ºC*	3.8	2.4	20 – 40

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
OSU, NU, ZTPlus, BSST

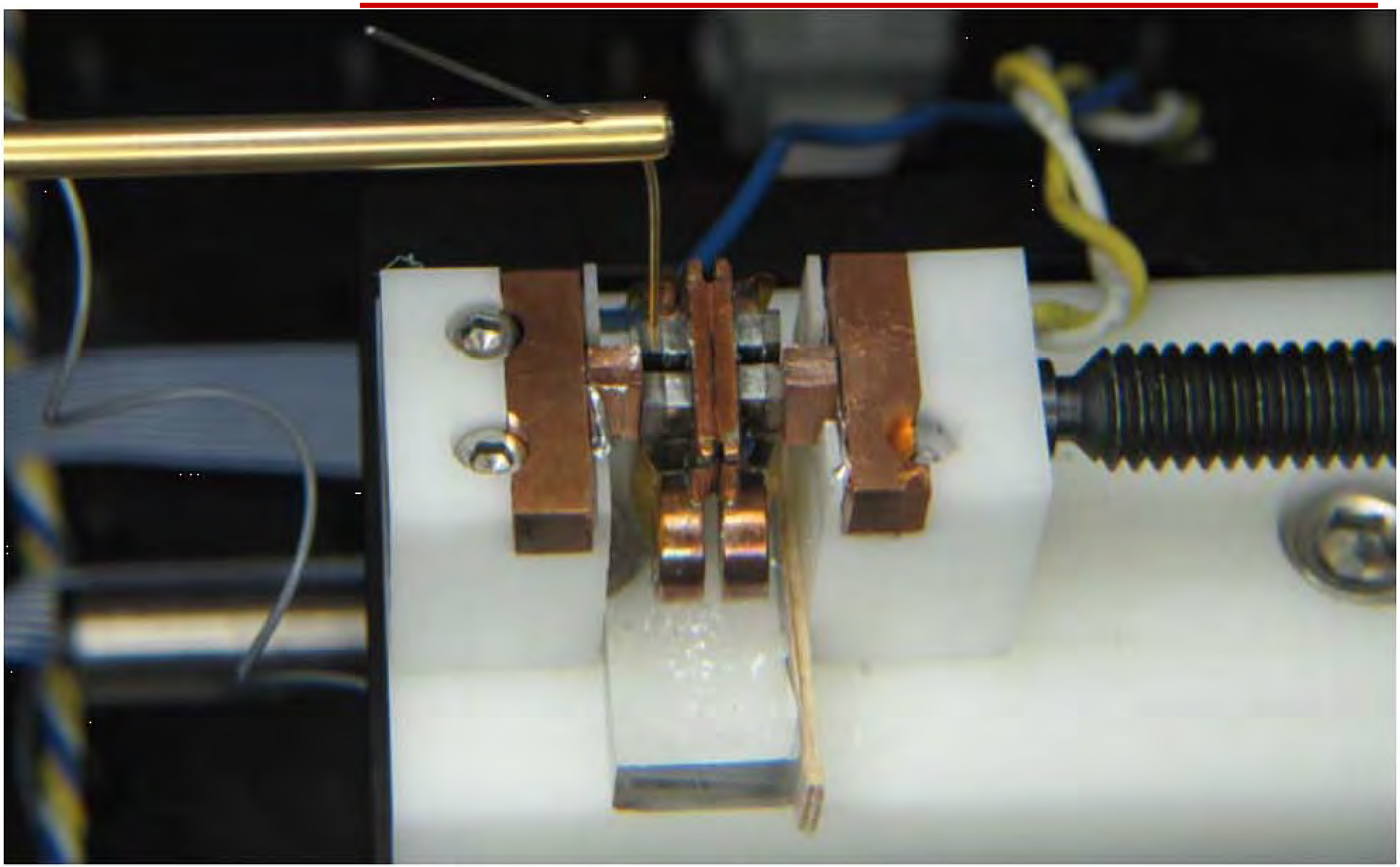
4.2 Electrical contact resistances
ZTPlus

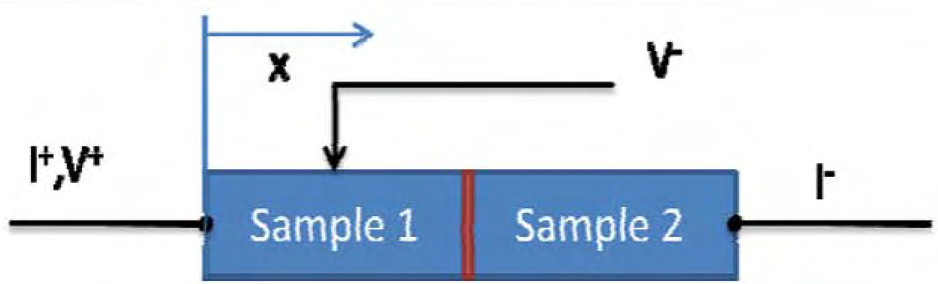
4.3 Thermal contact resistances (new technique) *Virginia Tech*

4.4 Device performance
BSST

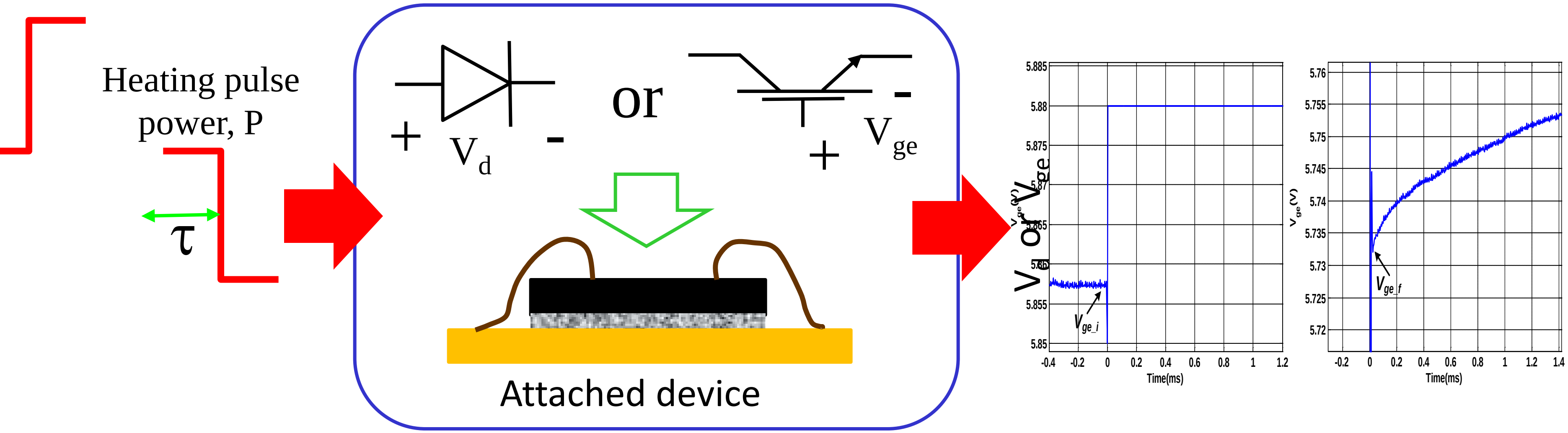
4.5 Circular cross-check is now possible
=> determination of the error bars

4.1 Electrical contact resistances





4.2 Thermal contact measurements



$$\text{Thermal impedance: } Z_{th} = \frac{\Delta T}{P_H} = \frac{\frac{\Delta V}{K}}{I_H V_H (1-\varphi)} = \frac{V_{Fi} - V_{Ff}}{I_H V_H (1-\varphi) K}$$

V_{Fi}: The initial VF value before application of heating power;
V_{Ff}: 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 IH to the DUT;
P_H: The heating power pulse magnitude; product of VH and IH;
K: Thermal calibration factor, in mV/^{o}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

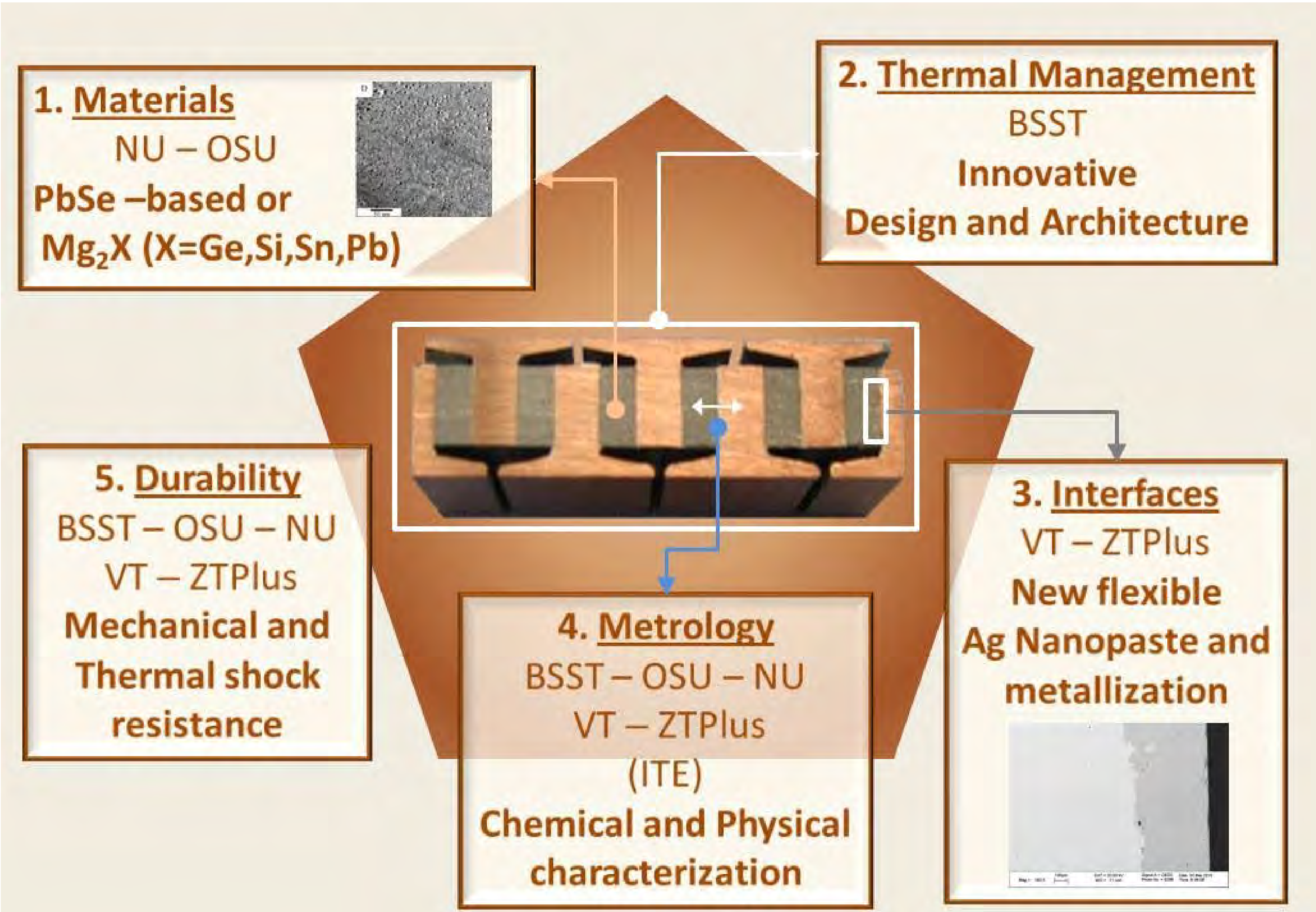
1. New Interface technologies
   1. Compliant highly conductive contacts, Ag nanopaste
   2. In-situ metallization during pellet consolidation
   3. Deposition techniques

- Metology
  – New thermal contact resistance measurement technqiue
  – Self-consistency check: materials/interfaces/devices

- Reliability
  1. Design-inherent
  2. Automotive-level durability testing

Supplemental slides

Approach



1. Materials
NU – OSU
PbSe –based or
Mg2X (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

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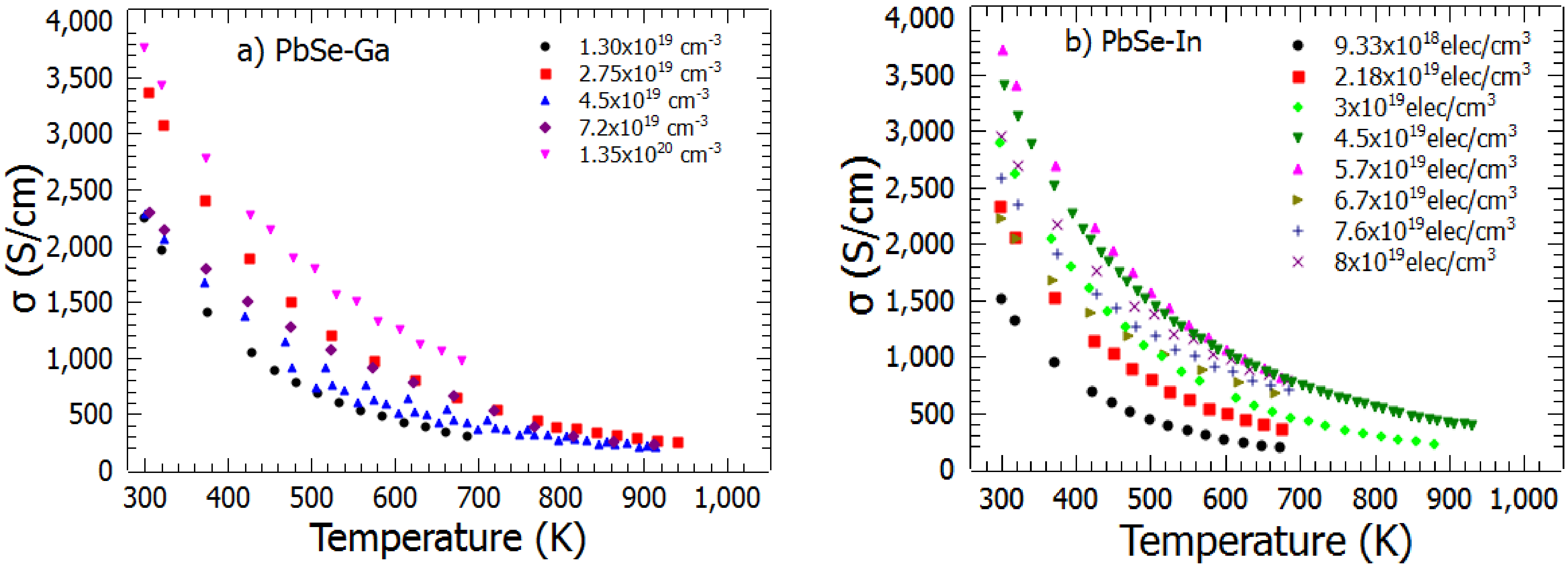
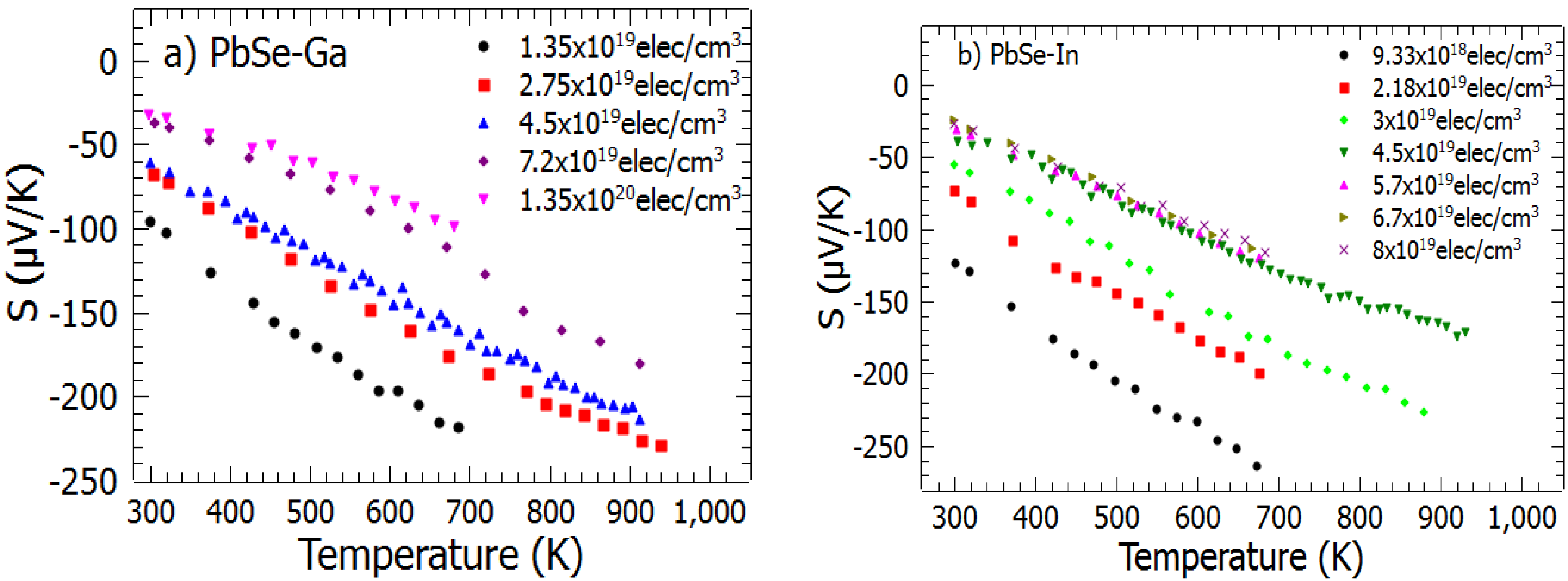
PbSe-In and PbSe-Ga results: electrical conductivity



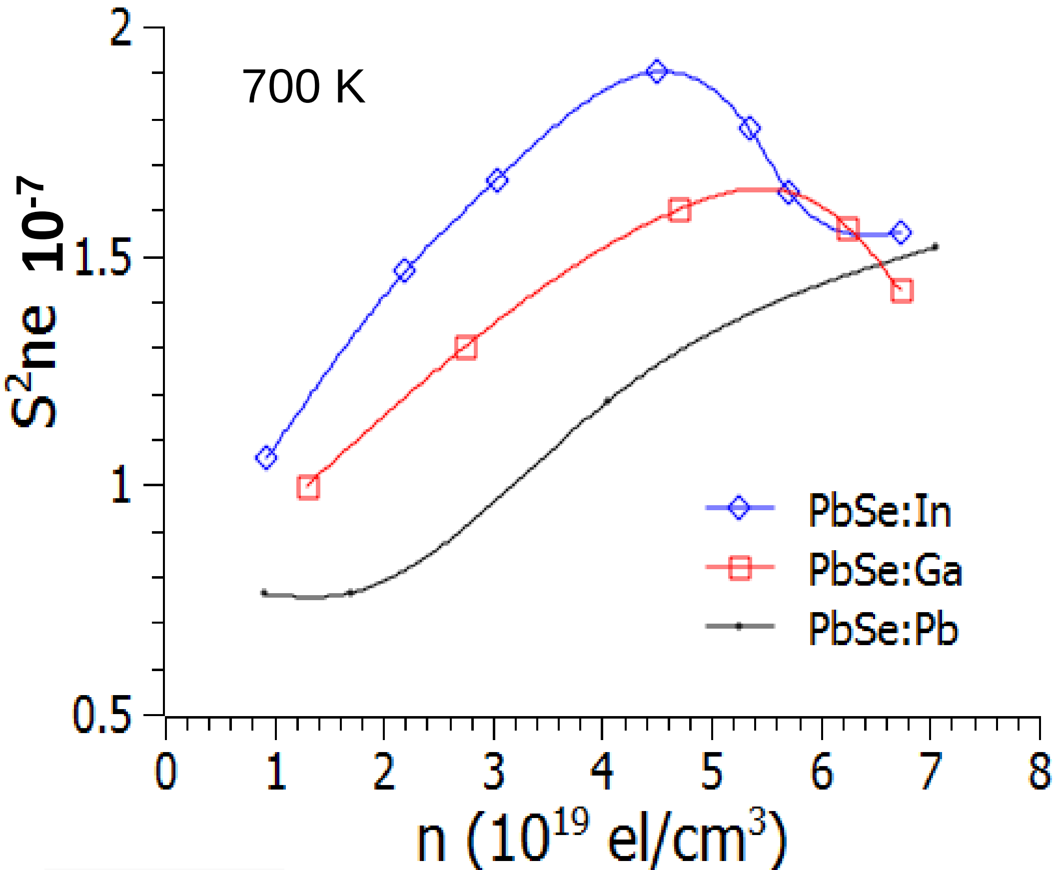
- Polycrystalline cast ingots
- Ga samples suffer from microcracks and other defects limiting mobility
- Both Ga and In efficiently generate carriers in PbSe

PbSe-Ga and PbSe-In: Seebeck



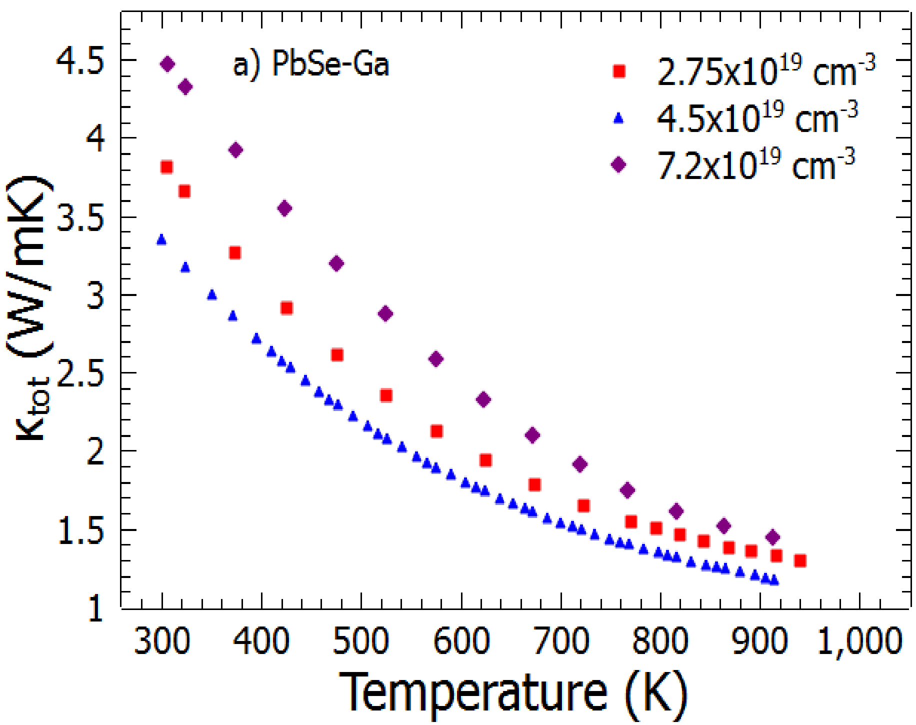
- Linear variation
- No saturation up to 900 K
- In doped samples have a higher thermopower at 700 K compared to Ga
- Reduced power factor (S^2ne) demonstrates the above

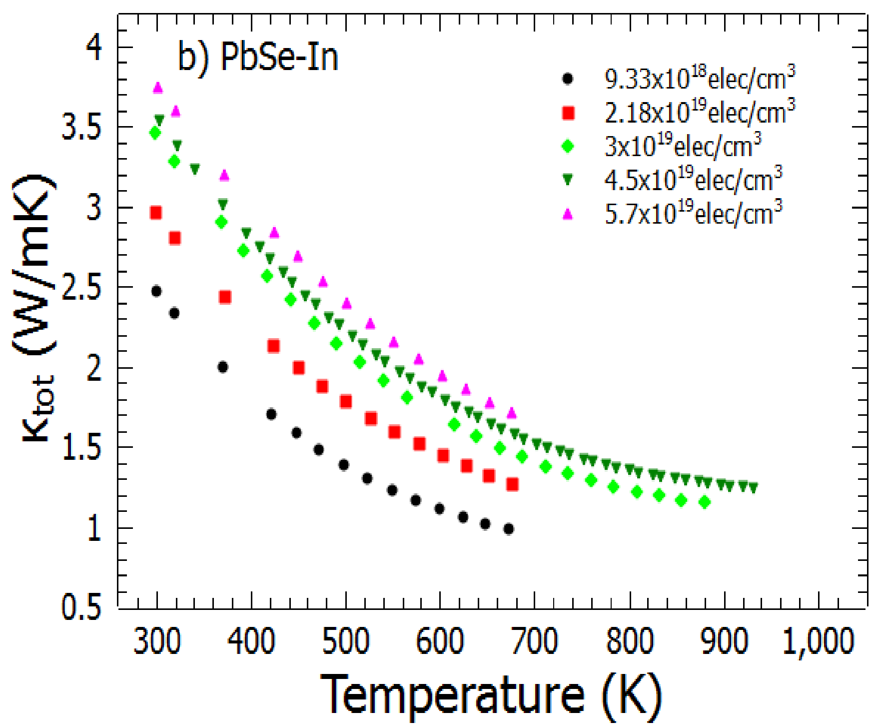
PbSe-Ga and PbSe-In: Reduced power factor 700K



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

Milestones

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

Milestones

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

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

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

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