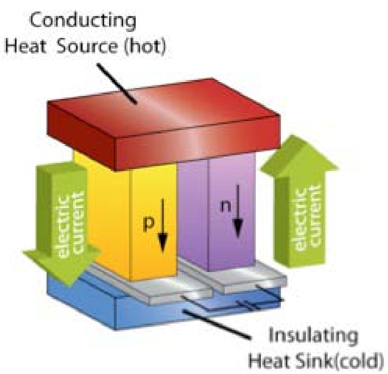
Ben-Gurion University of the Negev

Ilse Katz Institute for Nanoscale Science and Technology

Practical Considerations while Developing a Thermoelectric Energy Converter



Yaniv Gelbstein
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the *i*sraeli ThermoЄlectric Applications and materials group

Department of Materials Engineering
Ben-Gurion University
Beer-Sheva, Israel

2014 LETS
LEADING ENABLING TECHNOLOGIES FOR SOCIETAL CHALLENGES

SiNERGY

the SiNERGY Workshop organized within LET's Conference, Sept. the 30th ,
Palazzo della Cultura e dei Congressi, Italy

BSF United States – Israel Binational Science Foundation

SEVENTH FRAMEWORK PROGRAMME

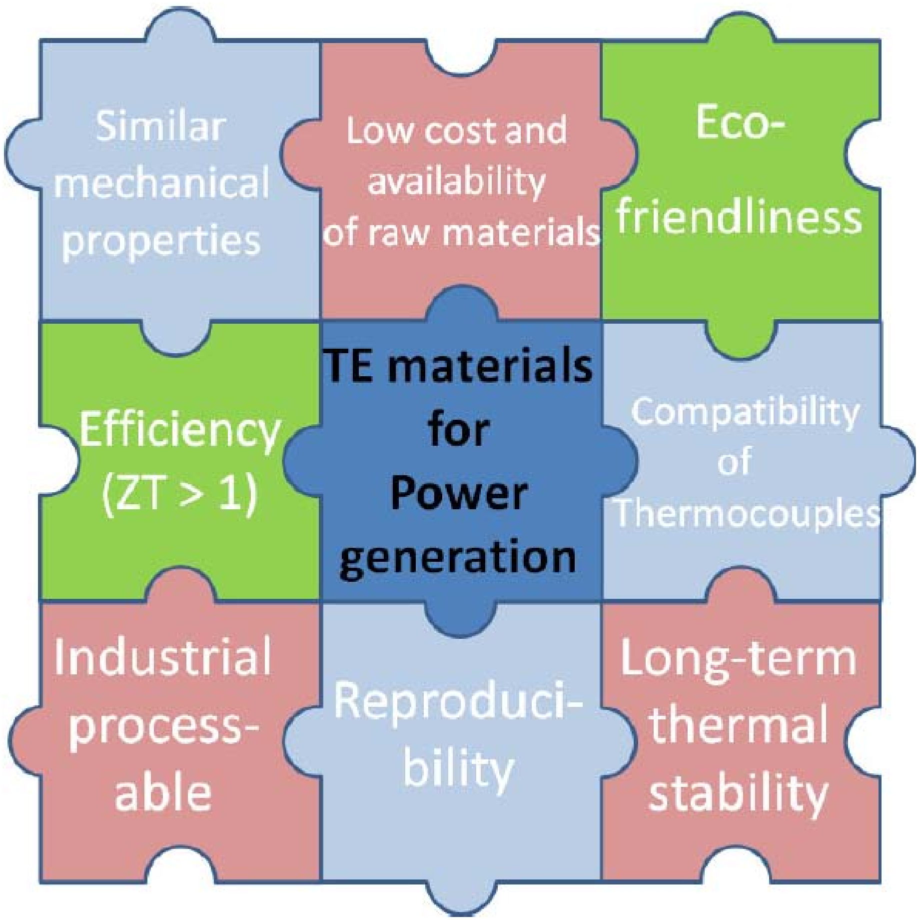
BOSCH Invented for life

vossloh

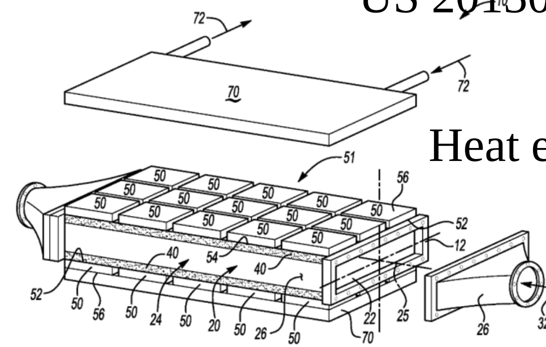
Fondation Adelis

מפא"ת

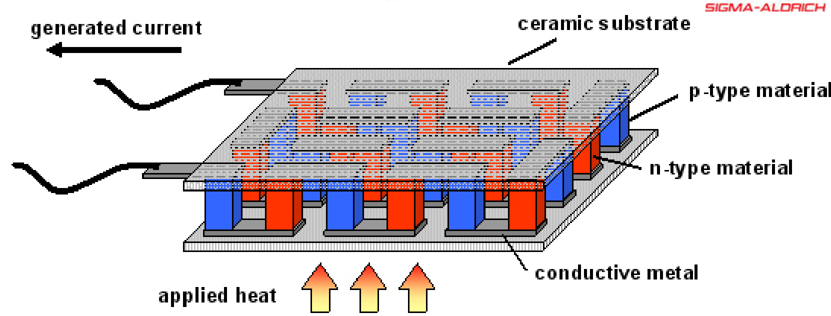
TE materials’ criteria for large-scale power generation

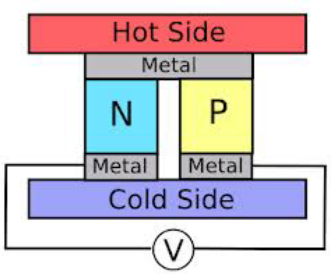


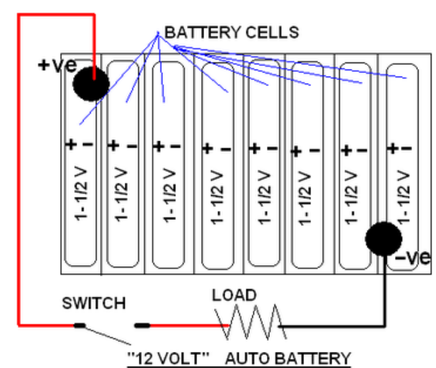
US 20130000285 A1



Heat exchangers

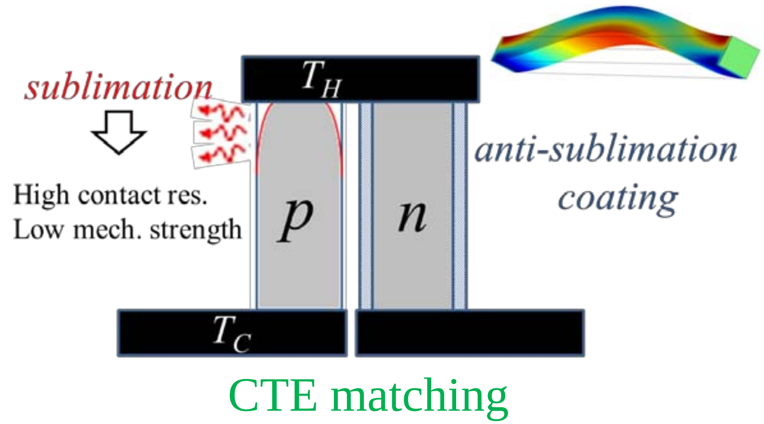






Julia Krez, Ph.D thesis, Johannes Gutenberg University, Mainz (2014)

Kilimanjaro

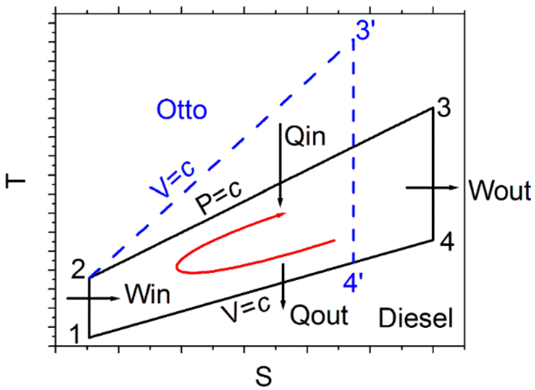


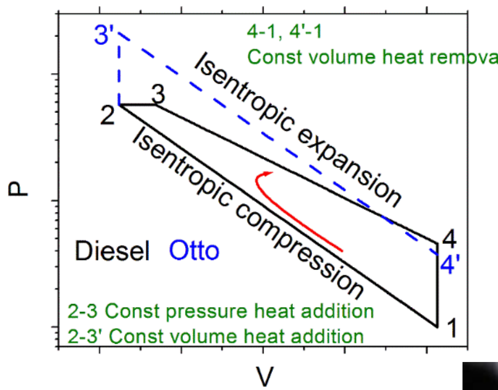
Dry ice ***sublimation***

oxidation

From mt. Everest, snow is constantly lost invisibly due to ***sublimation***

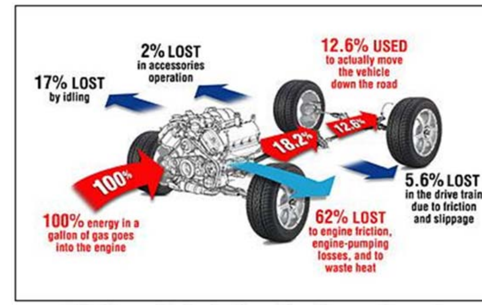
Otto (spark ignition) vs. Diesel (compression) cycles



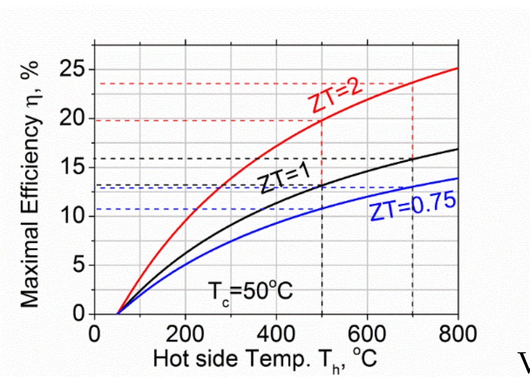


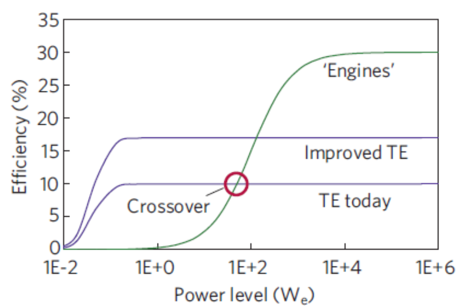
$$Same\ compression\ ratio\ -\ \left(\frac{V1}{V2}\right)_{Otto} = \left(\frac{V1}{V2}\right)_{Diesel}$$

$$Same\ Qin\ -\ \int_2^3 TdS = \int_2^{3'} TdS$$



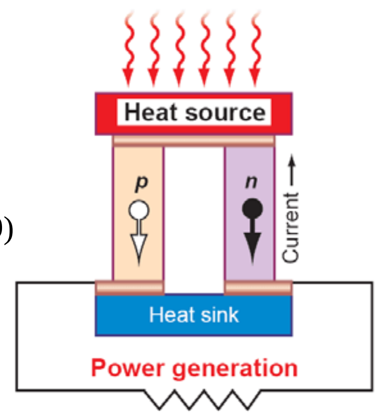
$Z=\alpha^2/\kappa\rho$

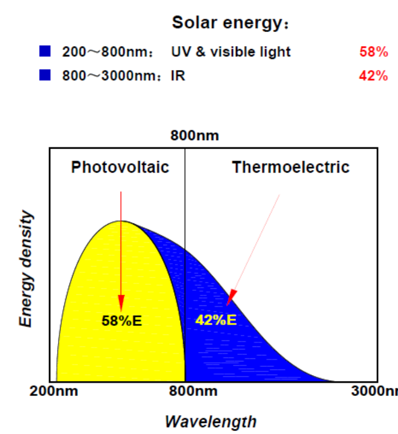




Vining, Nature Materials **8,** 83-85 (2009)

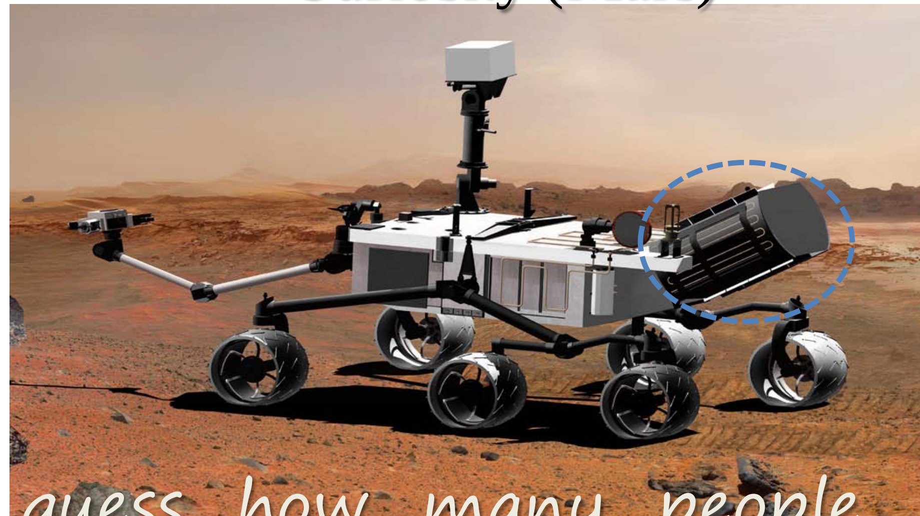
$$\eta_{opt} = \frac{\Delta T}{T_H}\frac{\left(\sqrt{1+Z\overline{T}}-1\right)}{\sqrt{1+Z\overline{T}}+\frac{T_C}{T_H}}$$





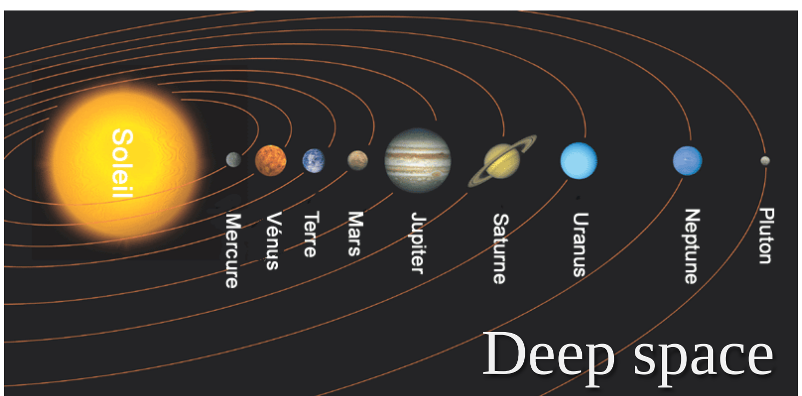
Apollo (Moon)

Curiosity (Mars)

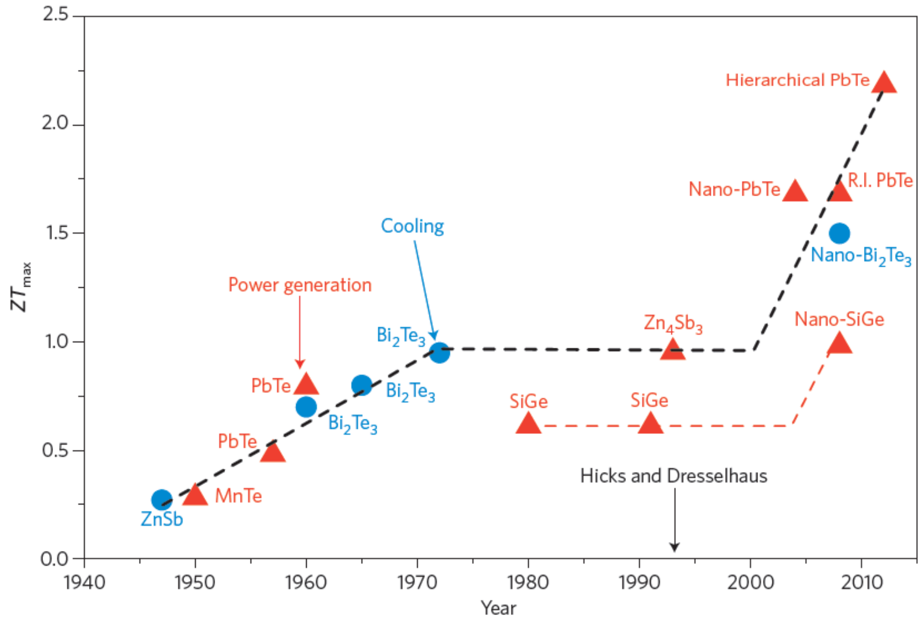


Can you guess how many people worked for NASA for developing of this technology?

November 26, 2011



Main requirement for Deep Space: Long Term Stability



Nature Nanotechnology **8** 471 (2013)

Closest distances to the Sun:

Venus : 107,400,000 km

Mercury : 45,900,000 km

Earth: 147,100,000 km

Mars : 207,000,000 km

Jupiter : 740,000,000 km

Saturn : 1,346,400,000 km

Uranus : 2,742,000,000 km

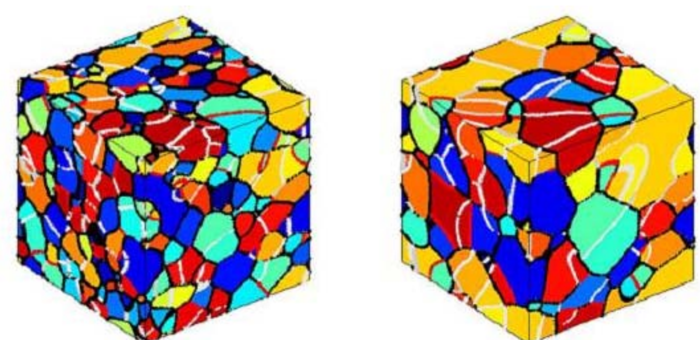
Neptune : 4,460,000,000 km

Pluto : 4,425,000,000 km

Is there any contradiction between nanstructuring & stability?

Further efficiency enhancement will Require both nanstructuring for efficient phonon scattering and electronic optimization for enhanced transport properties, combined with the required stability demands.

Coarsening / Nano-features growth



Using novel TE materials, a new generators technology should be developed?

PRL **101** 025502 (2018)

More "earthy" applications

POWERDRIVER

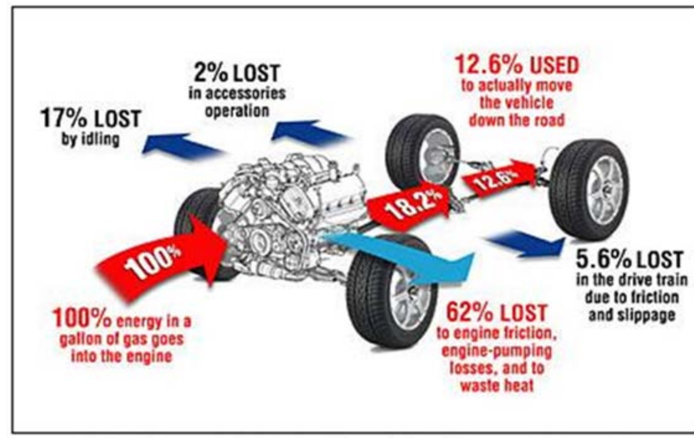
SEVENTH FRAMEWORK PROGRAMME

Grant agreement n°: 286503
Start and end dates: Feb. 2012-Feb. 2014
Coordinator: European Thermodynamics Ltd, UK, Kevin Simpson and Barri Stirrup, barri.stirrup@etdyn.com.
Consortium: Power Driver (13 partners - 5 RTDs, 6 SMEs and 2 Other Enterprises)

Partner	Beneficiary Name	Country	Role
1	**BGU** (Yaniv Gelbstein, Yossi Marciano)	Israel	**RTD** – Telluride Materials – synthesis / thermoelectric characterization
2	**IML** (Jonathan Tunbridge, Richard Dixon)	UK	**RTD**- Silicide Materials – synthesis / structural characterization
3	**QMUL** (Mike Reece, Huanpo Ning)	UK	**RTD**- Silicide / Telluride Materials – SPS / characterization
4	**JLR** (Robert Gilchrist)	UK	**Other Enterprisers and End Users**
5	**Halyard** (Richard Summers)	UK	**SME** – Marine.
6	**Tecnalia** (Iñigo Agote)	Spain	**RTD**- Silicide Materials – SPS / structural characterizations
7	**ETL** (Kevin Simpson)	UK	**SME** – TEG development / coordination
8	**Ricardo** (Cedric Rouaud, Peter Feulner)	UK and Germany	**RTD** – TEG / Heat Exchanger design and Manufacturing
9	**Nanoker** (Sergio Rivera, Ramon Torrecillas)	Spain	**SME** – Silicide Materials SPS up-scaling.
10	**Rolls Royce** (Mark Husband)	UK	**Other Enterprisers and End Users**
11	**Thermex** (Julian Crossley, Ivan Robinson)	UK	**SME** – Heat Exchanger
12	**DTS** (Marco Stella, Carlo Bonfreschi)	Italy	**SME**- Exhaust, Dissemination, automotive application
13	**FCT** (Jürgen Hennicke)	Germany	**SME**- SPS

Main Objectives

Development of thermoelectric generators in the range of **300-600W** output electrical power for **automotive** applications (gasoline engines) by utilizing the waste exhaust heat generated into useful electrical power. The project has also a target of more than **1.5kW** for **marine** (Diesel engines) applications such as leisure boats and several kW for Large Diesel/Gas engines.



JAGUAR

Halyard

Rolls-Royce

vossloh

Locomotives


Wuppertal, DE

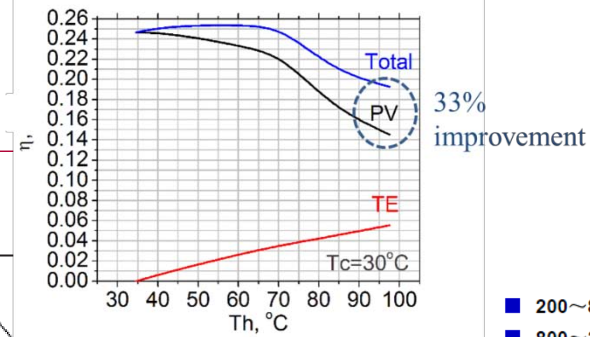
Passenger rail vehicles

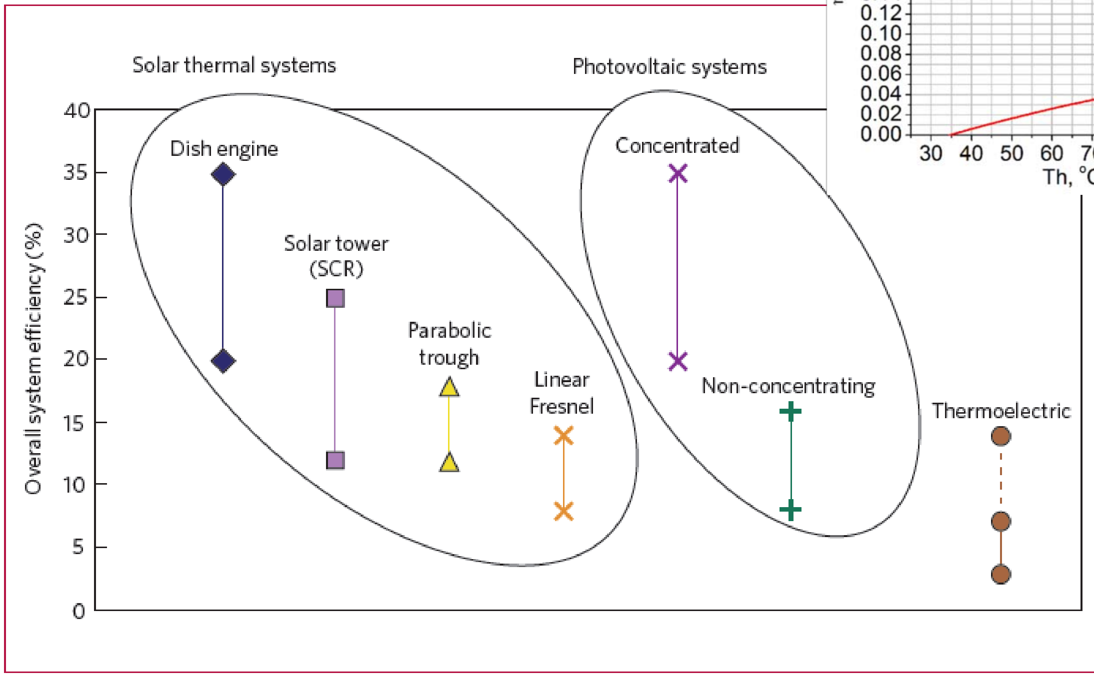
Tubelink

Citylink

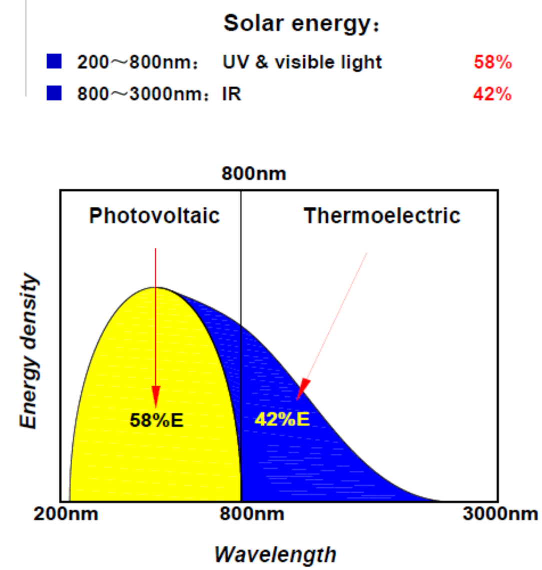
Tramlink

PV-TE applications

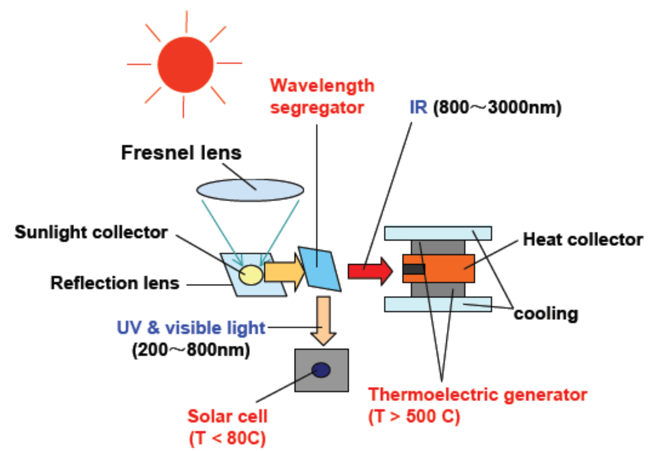




Kraemer et al., *Nature Materials* **10** 532-538 (2011)



Hybrid PV-TE system:



Collaboration with Prof. Eugene Katz, Dr. Ofer Beeri

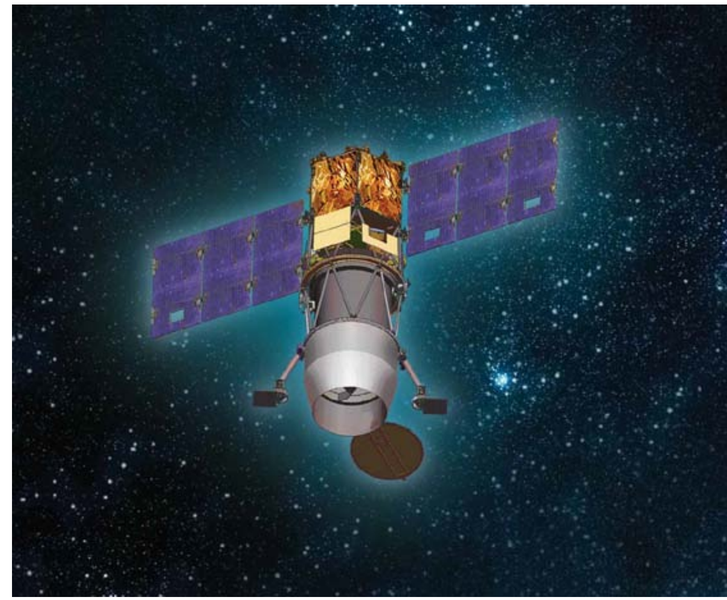
מפא"ת

ISRAEL DEFENSE FORCES

צבא הגנה לישראל

IAI

ISRAEL AEROSPACE INDUSTRIES



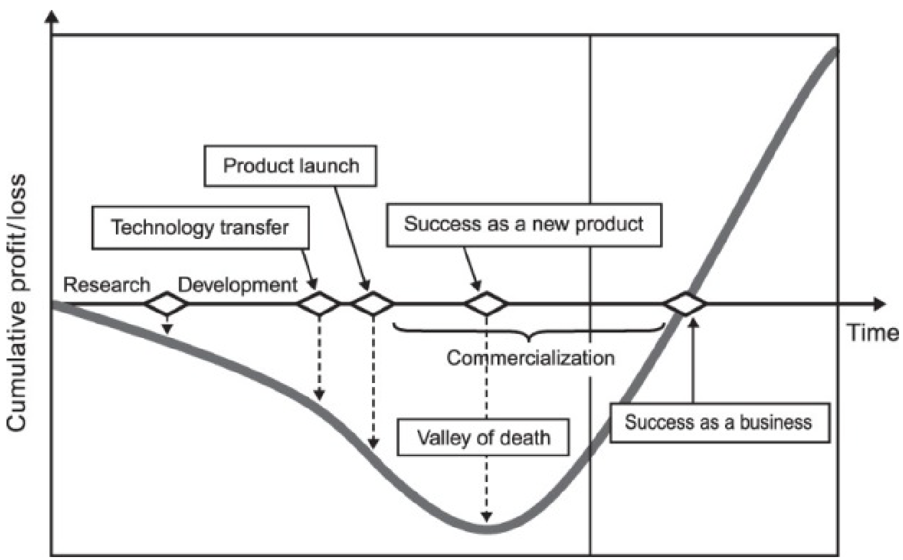
“Hybrid” Tank

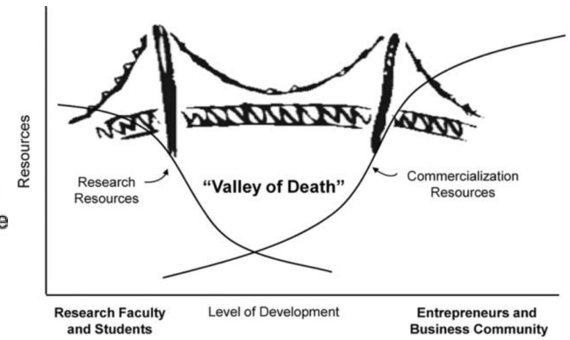
Satellites

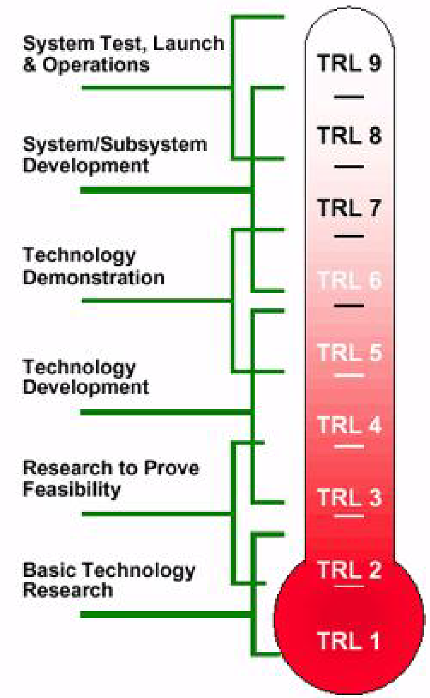
Project	Title	Coordinator/ presenter	comments
Subcluster 1 – TE bulk nanomaterials			
ThermoMag	Nanostructured energy harvesting thermoelectrics based on Mg_2Si	ESA / A. Amaldi	6.4M€/3.5y ZT~1.4(n), 0.5(p)
NexTEC	Next Generation Nano-Engineered Thermoelectric Converters – from concept to industrial validation	KTH, Sweden / M.Muhammed	6.4M€/3y Skutterudites (ZT~1.5), nano-Bi_2Te_3 (ZT~1.15)
NEAT	Nanoparticle embedded in alloys thermoelectrics	CEA, France / J. Simon	Si_xGe_{1-x} (Mo inclusions)- ZT~0.8, n-$Mg_2Si_{0.4}Sn_{0.6}$ (ZT~0.9)
Subcluster 2 – TE thin film nanomaterials			
NanoHitec	Nanostructured High-efficiency Thermoelectric Converters	Oerlikon / G. Span	Bi_2Te_3 flexible modules, Short term (8€/W), Long term (2-3€/W)
GreenSilicon	Generate renewable energy efficiently using nano - Si	Univ. Glasgow / A. Samanelli	Ge/SiGe superlattices Nano-fabrication (ZT~0.49)
H2ESOT	Sustainable Organic TE devices	Simon Woodward, Univ. Nottingham / ETL	Potential ZT~0.45 based on A. Kasiyan. Basic science – long term replacement of Bi_2Te_3
SiNERGY	Silicon Friendly Materials and Device Solutions for Microenergy Applications	Luis Fonseca, IMB-CNM (CSIC), Spain	4.8M€/(1/11/2013-31/10/2016) Power Microgeneration and Storage Novel Si technology materials
Subcluster 3 – TE systems			
NanoTEG	Smart integration of electronics	CEA / J. Simon	cooling
SMARTOP	Self powered vehicle roof	Fiat / M. Brignone	Commercial BiTe modules (Gentherm)
HeatRECAR	Waste heat recovery in light duty trucks *target - 1-2€/W modules, 2-3€/W system*	Fiat / M. Brignone	Filled skutterudites (ZT~1(n),0.5(p)) and comerical BiTe modules
PowerDriver			

For PV – www.eupvclusters.eu. For TE – on the way.

1st EU Nano4Te Cluster Workshop, September 17th 2013, host event of the EMRS 2013 Fall Meeting, Warsaw University of Technology, Warsaw, Poland.







Technology Readiness Level (TRL)

The participated TE projects in the cluster are mainly in the TRL level of 3-5.
Future projects should be focused on getting beyond TRL of 5 or passing through the *valley of death*.

EUROPEAN COMMISSION

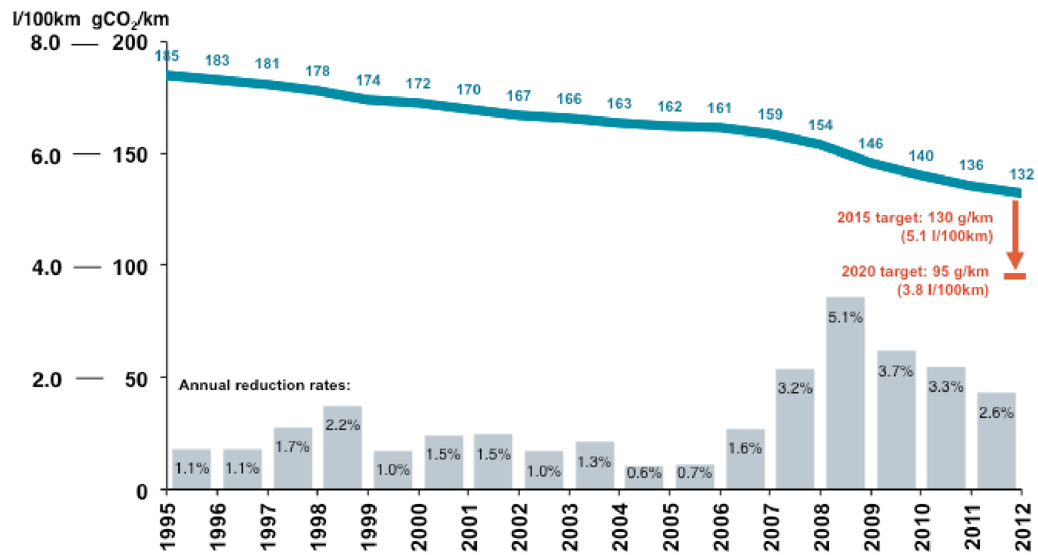
EU New Car CO_2 Regulation

To achieve their 20% reduction in total CO_2 emissions by 2020 from a 1990 base, the EU has adopted the New Car CO_2 Regulation. This sets out to deliver pan-European sales-weighted average new car CO_2 figure of 130g/km by 2015 and 95g/km in 2020. The 2020 target is a 45% reduction from 2007.

Manufacturers each face their own specific target, which includes a weight based element to reflect the different composition of manufacturers' fleets. Manufacturers can use super-credits and eco-innovations to help meet targets and can apply for a derogation if they are a small-volume or niche producer.

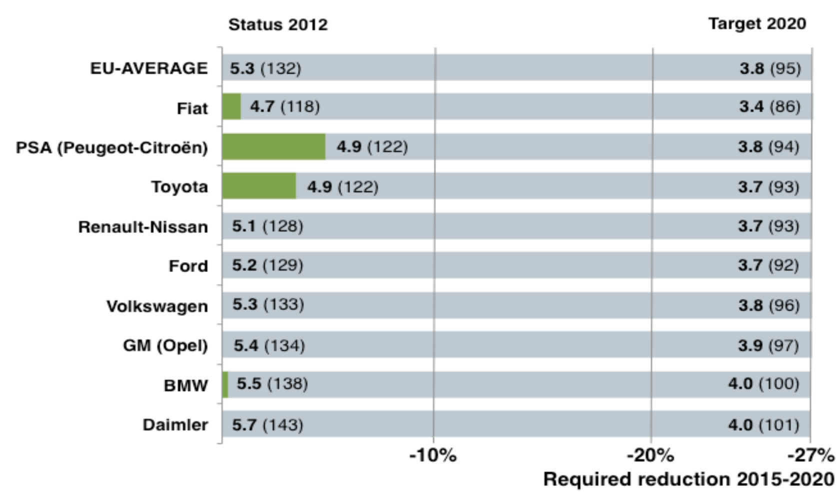
If targets are missed then penalties apply – of up to €95 for each gram CO_2 missed multiplied by the EU-wide registration volume. The 2015 target includes a phase-in, so 65% of the manufacturer fleet must meet their target by 2012, 75% by 2013, 85% by 2014 and 100% by 2015.

Average CO_2 emissions of new passenger cars in the EU
… in grams per kilometer (and liters fuel consumption per 100 kilometer)*



Sources: EU CO2 monitoring (EEA), ACEA.

Average fuel consumption in the EU by vehicle manufacturer
… in liters per 100 kilometer (and grams CO_2 per kilometer)*



Source: European Environmental Agency (2012 data). Calculation of 2015 and 2020 values assume no changes in vehicle weight and a CO2 conversion factor of 2.5 kg per liter.

The 2020 targets were established during a political process involving the European Parliament and Council.

NMP 16 – 2015: Extended in-service life of advanced functional materials in energy technologies (capture, conversion, storage and/or transmission of energy)

Specific challenge: Functional materials are enabling the large scale market penetration of secure, sustainable and affordable energy based on low-carbon, decentralised power generation. The benefits of using advanced functional materials can often be demonstrated in terms of, e.g., more efficient energy generation, storage or transmission, under controlled conditions. The high up-front investment costs of new power plants requires lifetimes of the order of 20 to 25 years, with minimal down and service time. However, not enough is known about the degradation of such materials during long-term service. This can seriously hamper the industrial uptake of such materials, increase initial investment costs due to the over-specification of the material requirements; or increase the exploitation costs, either by increased downtimes due to materials related failure or because of more intensive maintenance schedules.

Scope: Proposals should investigate the long-term in-service degradation of functional materials that have already demonstrated enhanced performance in terms of energy capture, conversion, storage and/or transmission, and the capability of a production at a scale that could warrant an industrial uptake. Proposals must include relevant modelling and testing under realistic conditions at pilot level. They should focus on improving the practical understanding of long-term in-service degradation on the performance of the functional material and its impact on the overall performance of the technology components and systems. The development of improved materials solutions, as well as relevant roadmaps and a catalogue of good practices, should be included.

Activities expected to focus on Technology Readiness Level 6.

The Commission considers that proposals requesting a contribution from the EU between EUR 6 and 10 million would allow this specific challenge to be addressed appropriately. Nonetheless, this does not preclude submission and selection of proposals requesting other amounts.

Expected impact:

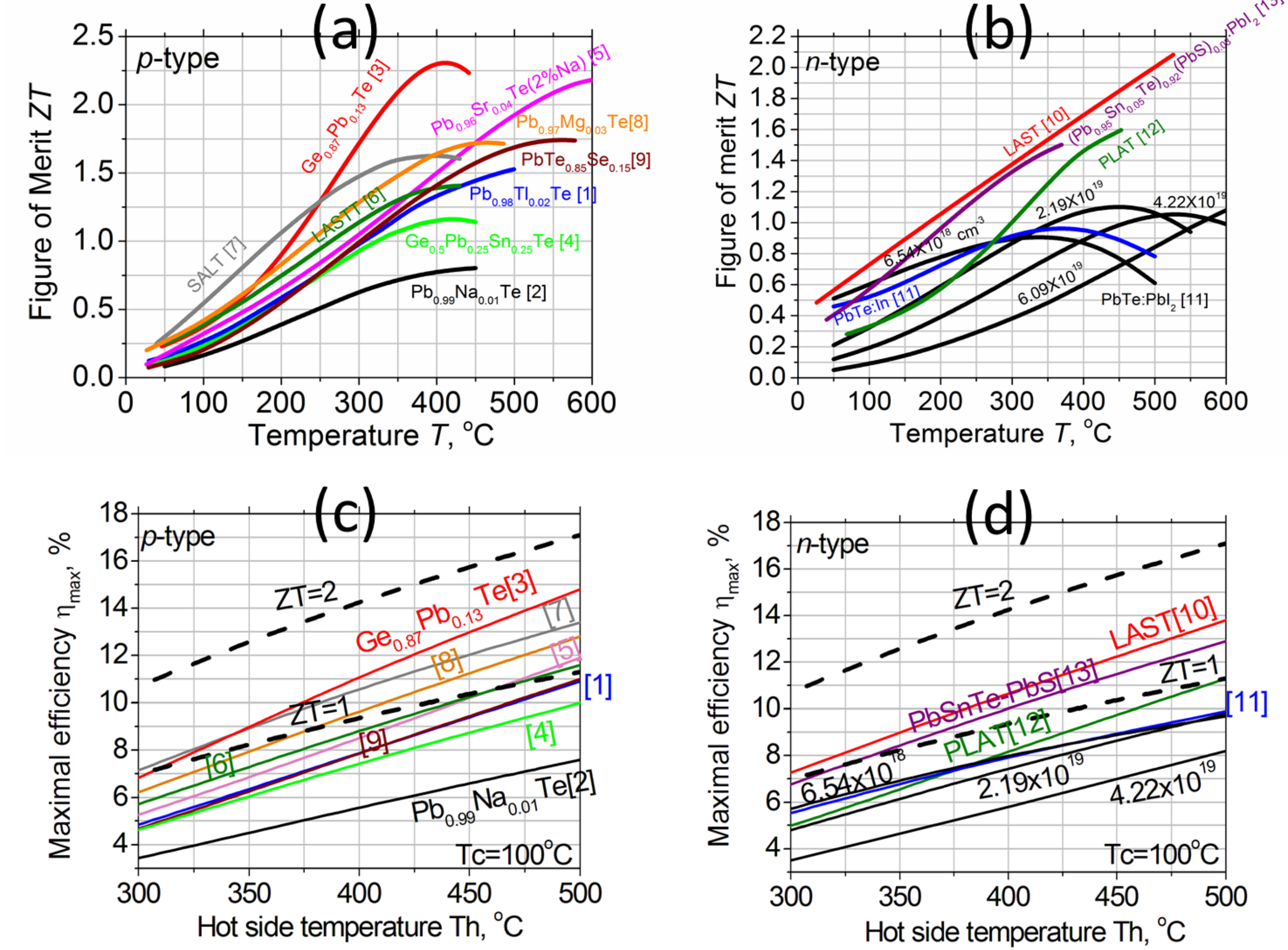
- Reduction of the capital (CAPEX) and/or operating (OPEX) expenditures in specific low carbon energy technologies;
- Implementation of relevant parts of the Materials Roadmap Enabling Low Carbon Energy Technologies (SEC(2011)1609); and relevant objectives of the SET-Plan (COM(2009)519).

Type of action: Innovation Actions

The conditions related to this topic are provided at the end of this call and in the General Annexes.

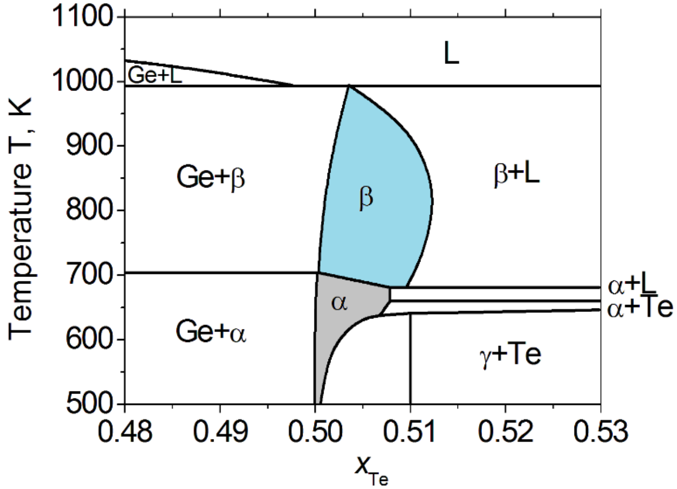
Call identifier	Type of Action	Budget (M Euro)	Deadline 2014	Deadline 2015
Nanotechnologies, advanced Materials and Production –	NMP – Two Stage RIA + IA and CSA (2 stage) NMP Topics (2014): 10,13,18,20,21,26,28,35 NMP Topics (2015): 11,12,15,16,19,22,23,24,29,30	114.2 (2014) 152 (2015)	Stage 2 7.10.14	Stage 1 26.3.15 Stage 2 8.9.15
	NMP– Single Stage RIA, IA and CSA (1 stage) NMP Topics (2015): 2,3,6,7	66.2 (2014) 66 (2015)	Closed	26.3.15
	CSA (single stage) NMP Topics (2015): 32, 38, 40	12.5 (2014) 2.65 (2015)	Closed	26.3.15
	NMP GV – 2014 NMP 17 (single stage)	16	7.10.14	–
	ERA-NET-2015 NMP 14 (single stage)	10	–	26.3.15

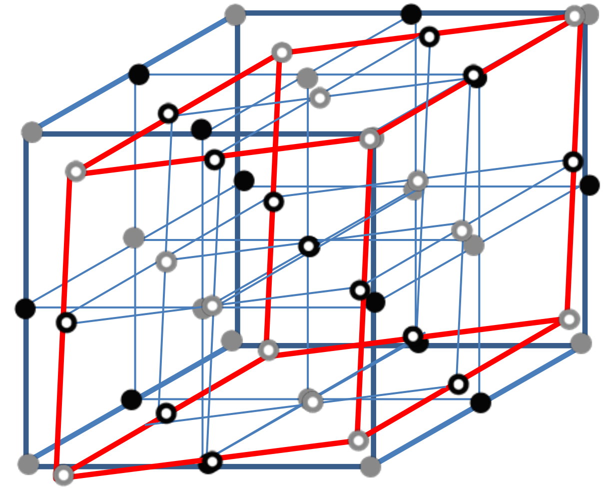
IV-VI



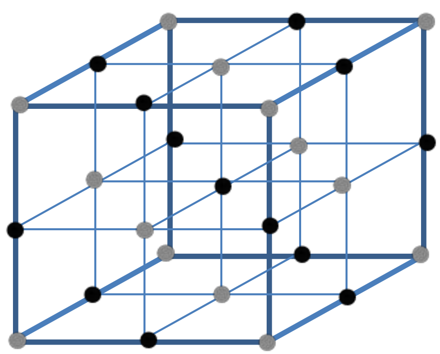
3. Yaniv Gelbstein, Mercouri Kanatzidis et al., *Adv. Energy Mater.* **2013**, *3*, 815–820 {Recent suppl. Data - *J. Am. Chem. Soc* **136** 11412-11419 (2014)}

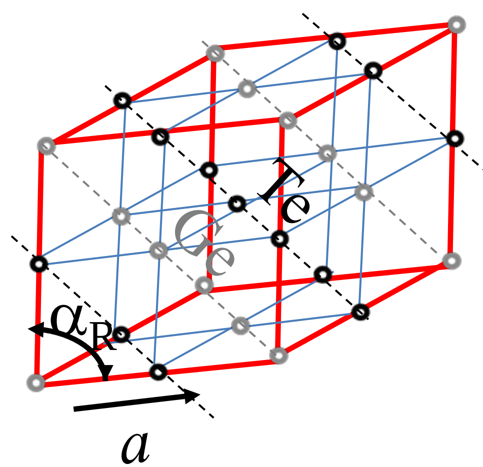
13. John Androulakis et al., *J. Am. Chem. Soc.* **129** 9780-9788 (2007)

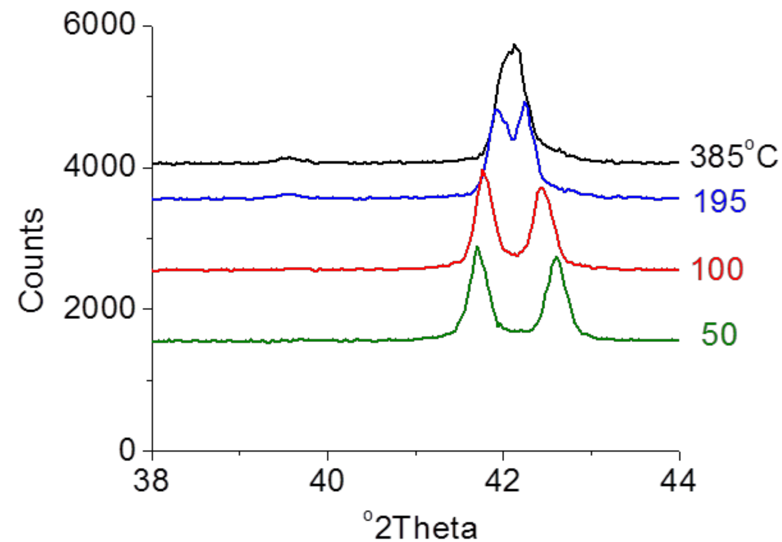




A. Schlieper et al., *Calphad* **23**(1) 1-18 (1999)



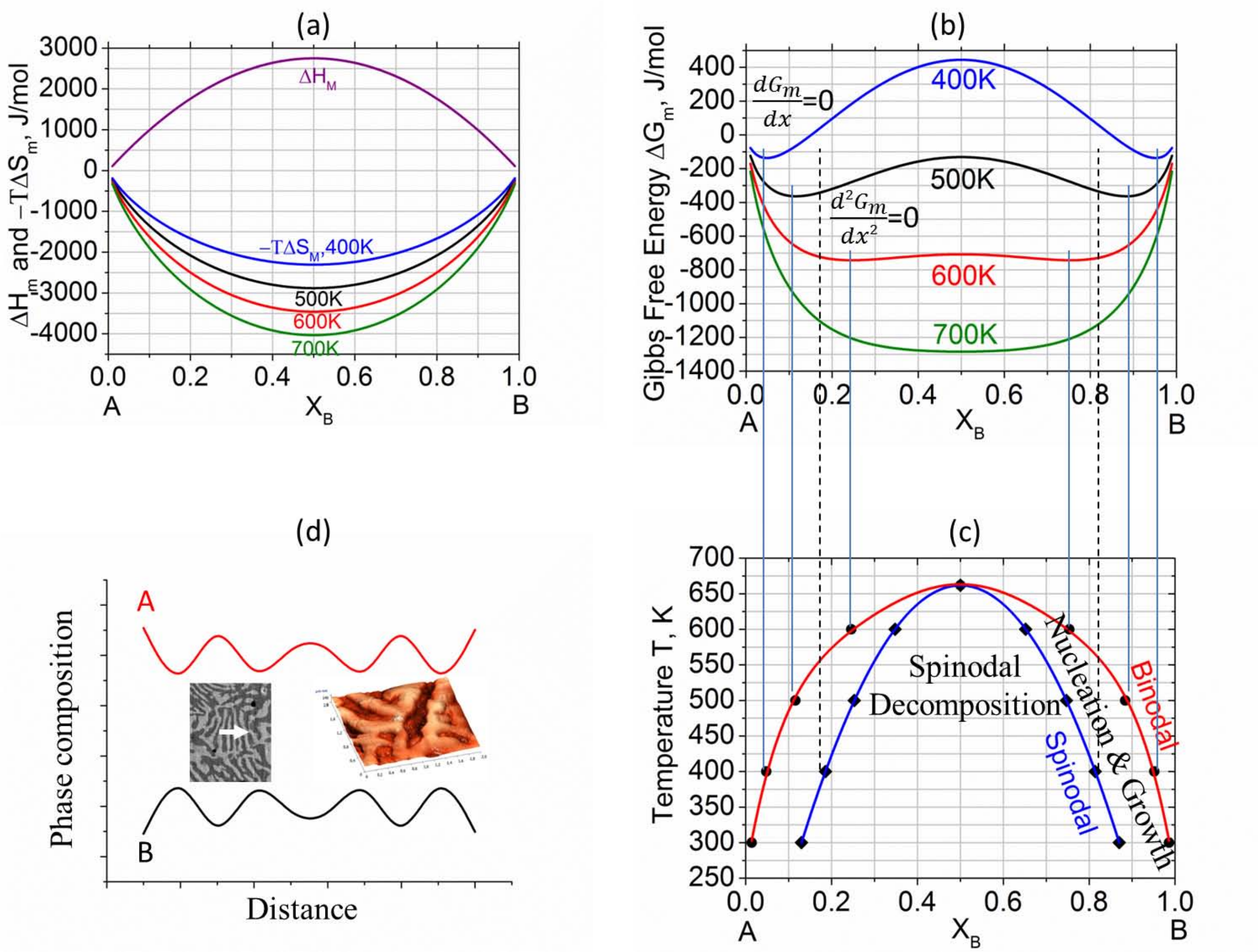




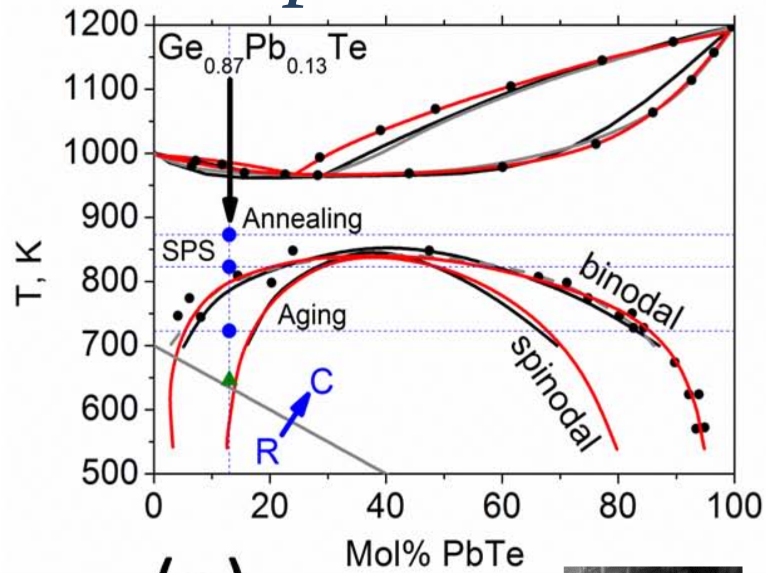
Phys.Stat.Sol. (RRL) **1**(6) 232-234(2007), *Powder Diffraction* **23**(2) 137(2008), *JEMS* **38**(7) 1478(2009), *Journal of Crystal Growth* **311** 4289(2009), *Chemistry of Materials* **22**(3) 1054 (2010), *JEMS* **39**(9) 2049,2165(2010), *Scripta Materialia* **62**(2) 89 (2009), *J. Phys. Chem. C* **114** 13126(2010), *J. Alloys and Compounds* **526** 31(2012), *JEMS* **42**(7) 1542(2013).

Phase Separation - I

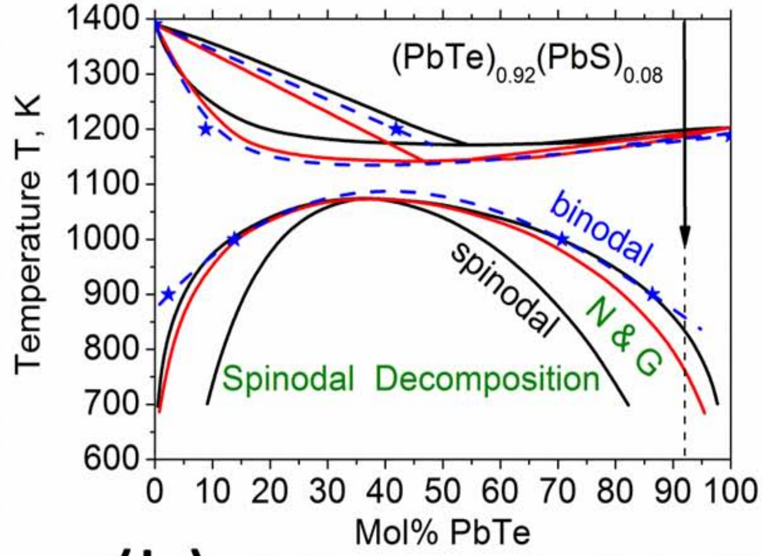
$$\Delta G_m = \Delta H_m - T\Delta S_m = \omega \cdot x \cdot (1-x) + T \cdot R \cdot [(1-x) \cdot ln(1-x) + x \cdot ln(x)]$$



Phase Separation - II

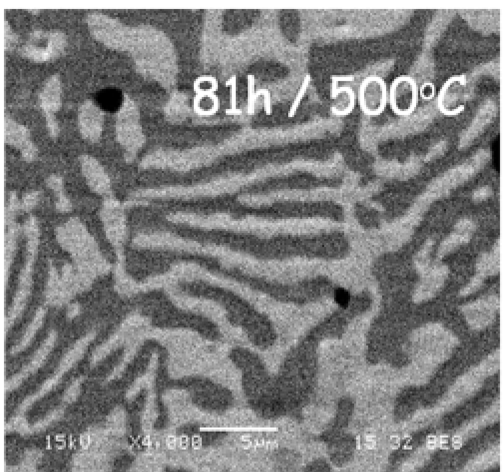


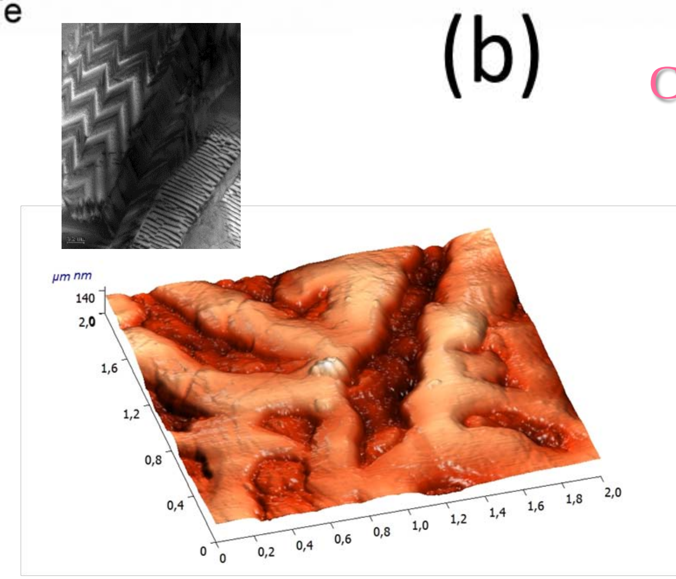
(a)

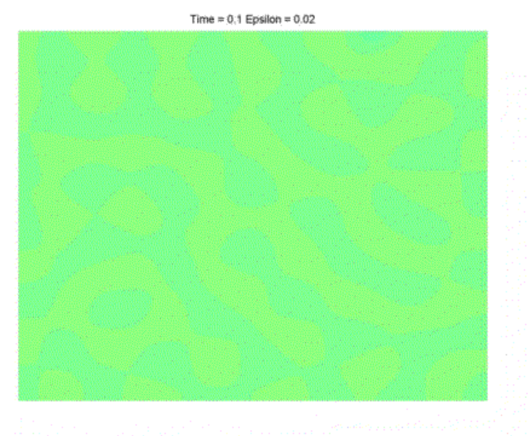


(b)

Cahn-Hilliard equation→



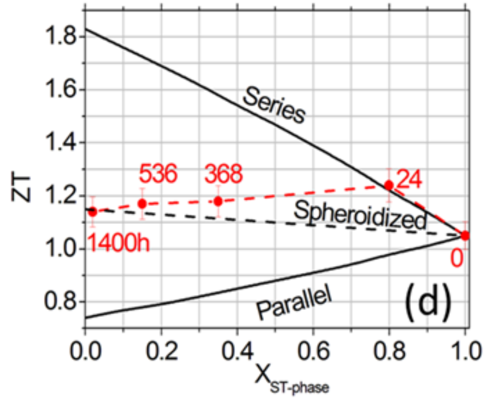


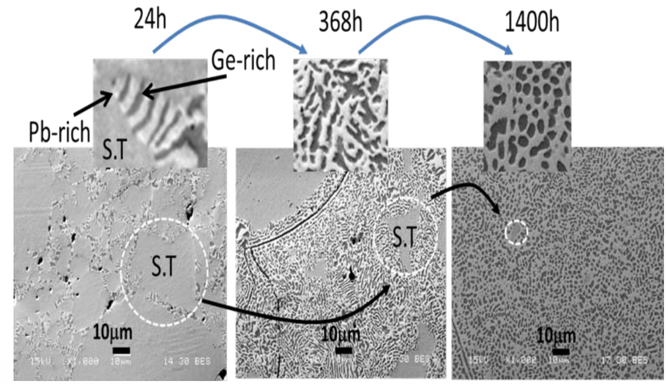


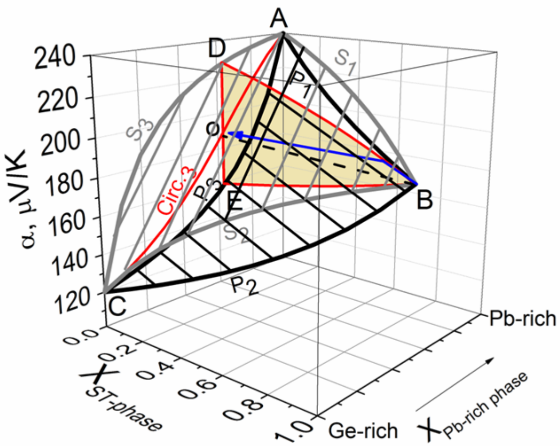
Evelyn Sander and Thomas Wanner, Monte-Carlo simulation

(a) Yaniv Gelbstein, Mercouri Kanatzidis et al., *Adv. Energy Mater.* **3** 815-820 (2013)

(b) John Androulakis et al., *J. Am. Chem. Soc.* **129** 9780-9788 (2007)







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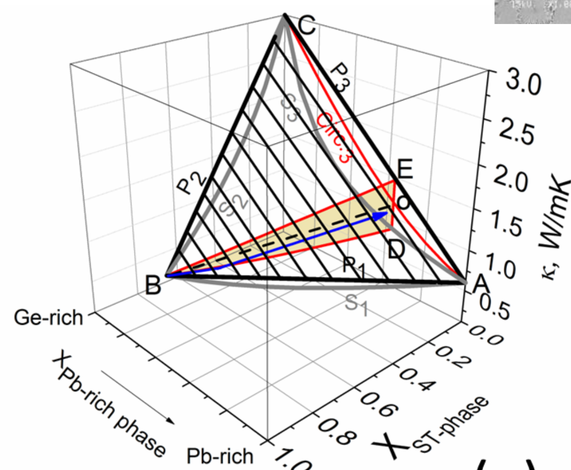

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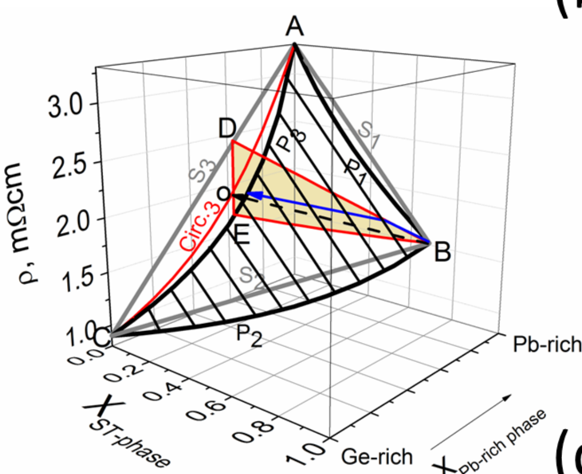

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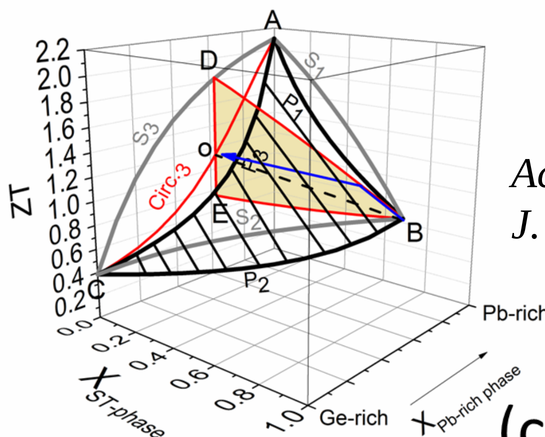
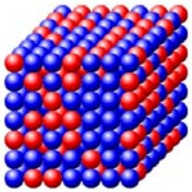


(c)

Acta Materialia **61** 1499–1507 (2013)
J. Appl. Phys. **112**, 113721 (2012)

Alloying Effects



Large F are required !!!

$$Z = \frac{\left(\frac{5}{2} + b - \eta\right)^2}{\left(2\frac{k^2}{e} FG \cdot \exp\eta\right)^{-1} + \left(\frac{5}{2} + b\right) T}, \quad F = \frac{\mu}{\kappa_l}\left(\frac{m^*}{m_0}\right)^{3/2}, \quad G = \left(\frac{2\pi m_0 k T}{h^2}\right)^{3/2}$$

"*alloy scattering*"

in solid solutions an additional carriers scattering mechanism is introduced due to the random distribution of different atoms in the same lattice site.

In the absence of nano-features, the reduction of the lattice thermal conductivity in A_xB_{1-x} solid solution alloys, $\kappa_{l,alloy}$, compared to the pure involved compounds, $\kappa_{l,pure}$, due to only umklapp and alloying/disordering point defects, can be predicted using:

$$\frac{\kappa_{l,alloy}}{\kappa_{l,pure}} = \frac{arc\tan(u)}{u}, \quad u^2 = \frac{\pi \cdot \Theta_D \cdot \Omega}{2\hbar \cdot \nu^2} \cdot \kappa_{l,pure} \cdot x(1-x)\left[\left(\frac{\Delta M}{M}\right) + \varepsilon\left(\frac{\Delta a}{a}\right)^2\right]$$

ε

γ

α- the linear thermal expansion coefficient (CTE)

r- Poisson's ratio

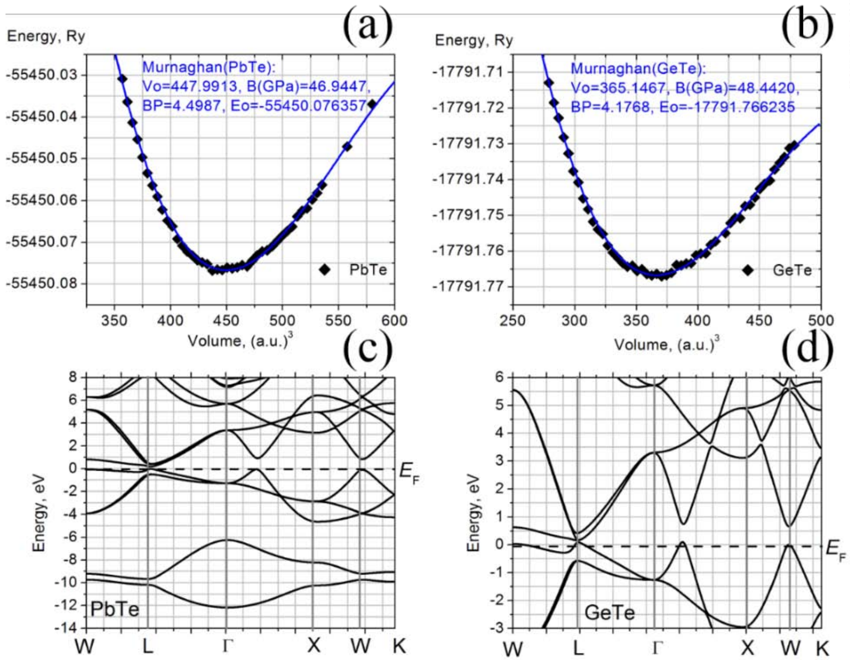
B- Bulk modulus

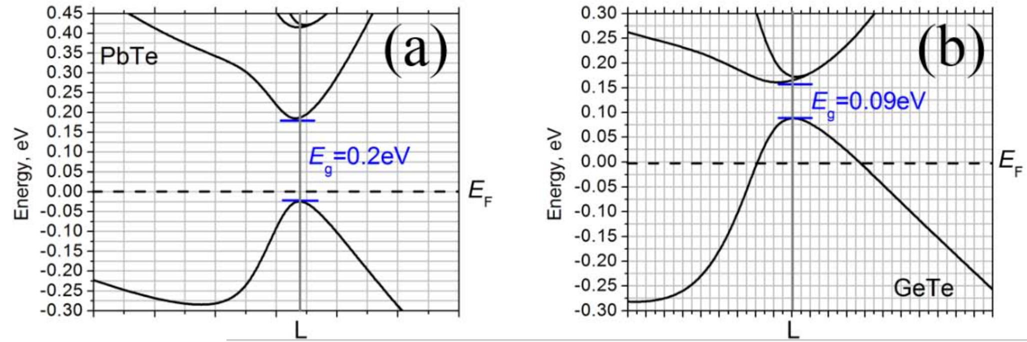
γ- Grüneisen parameter

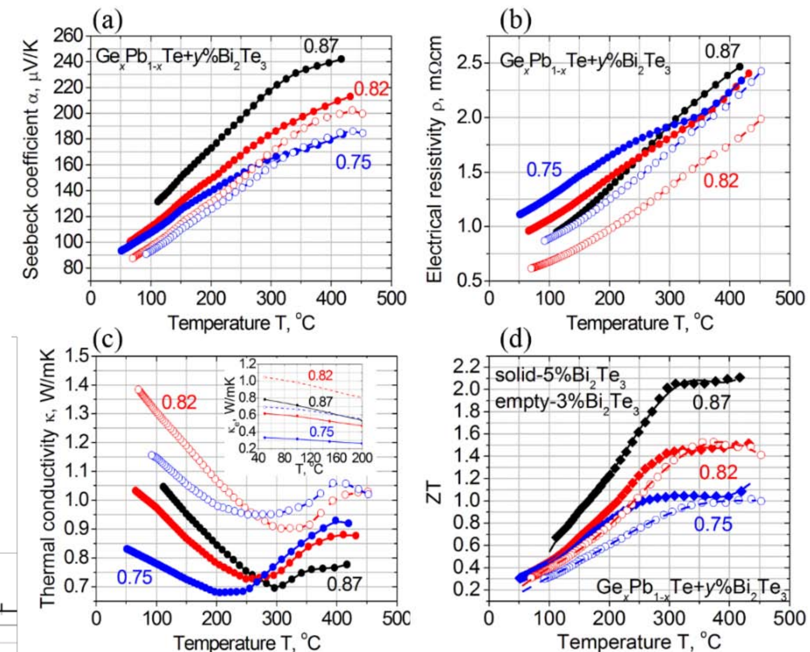
κ_l

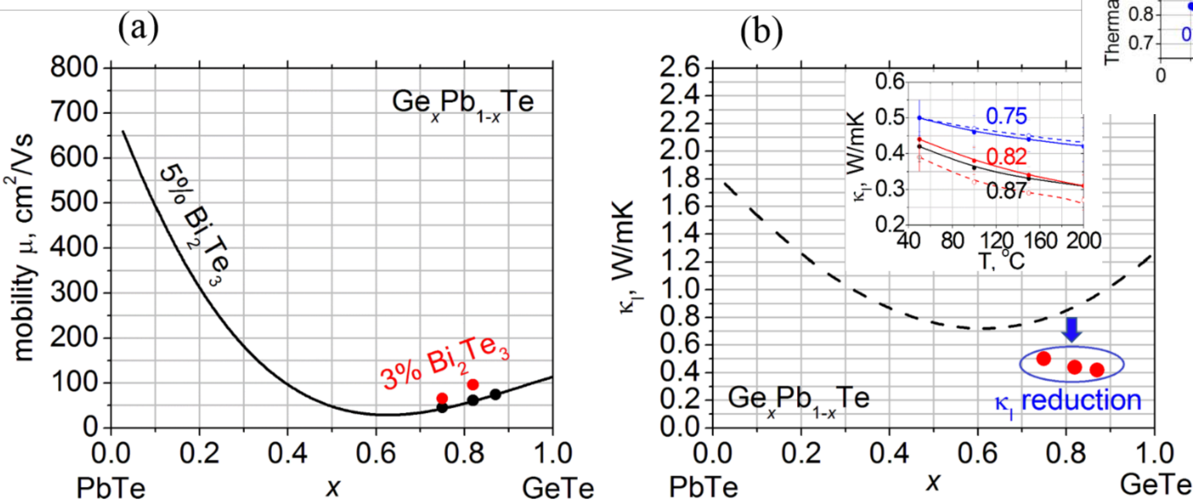
Physica Status Solidi B **251**(7) 1431-1437 (2014).

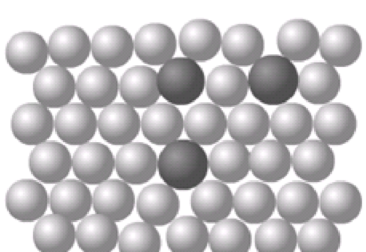
$Ge_xPb_{1-x}Te$ γ

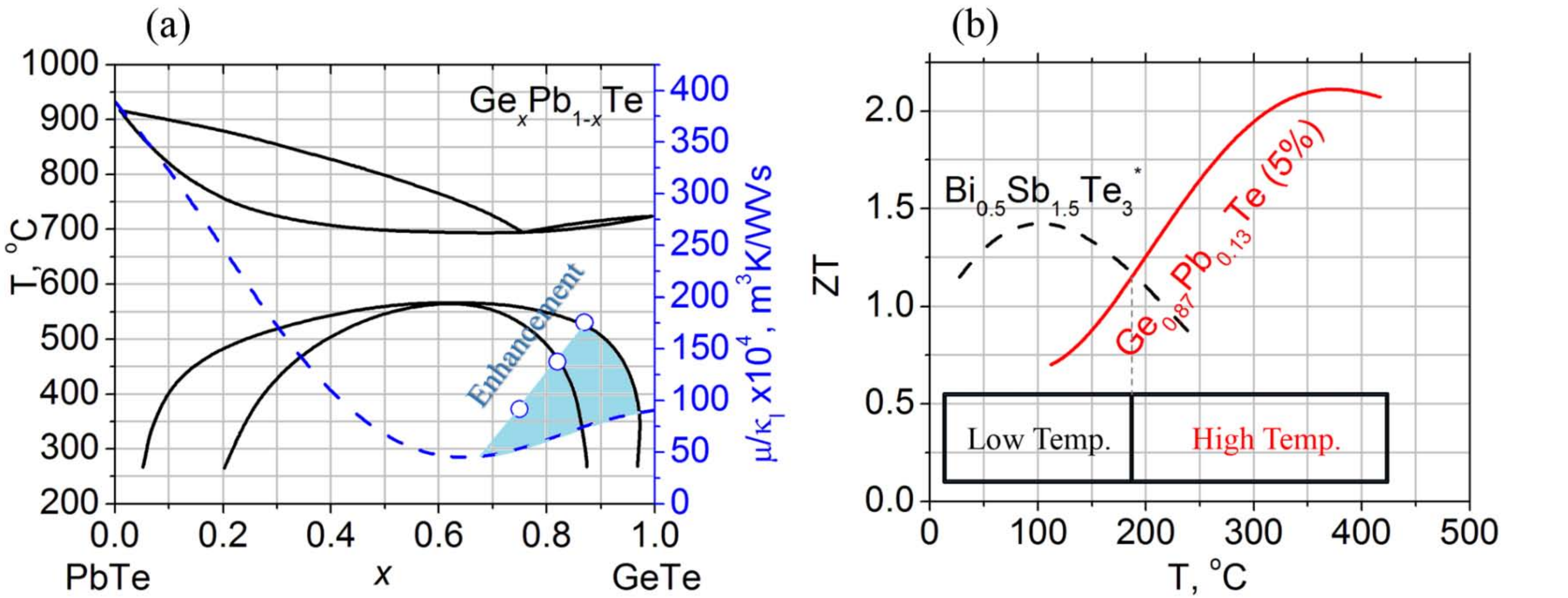


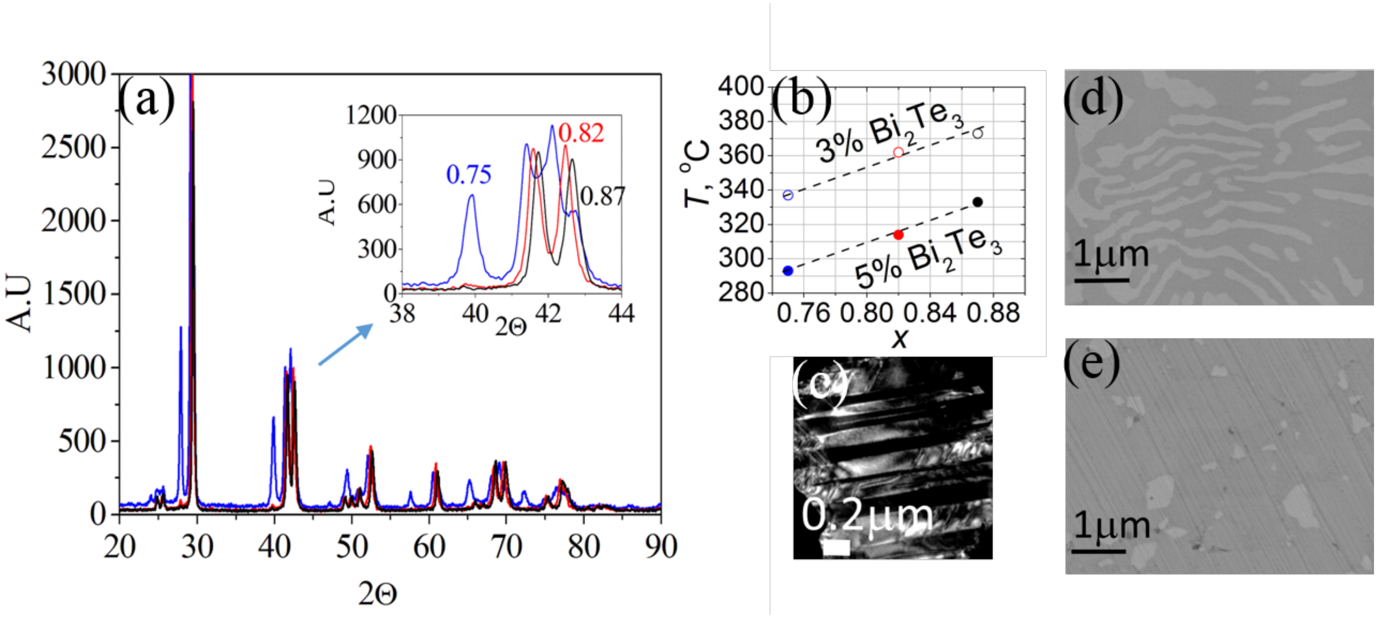










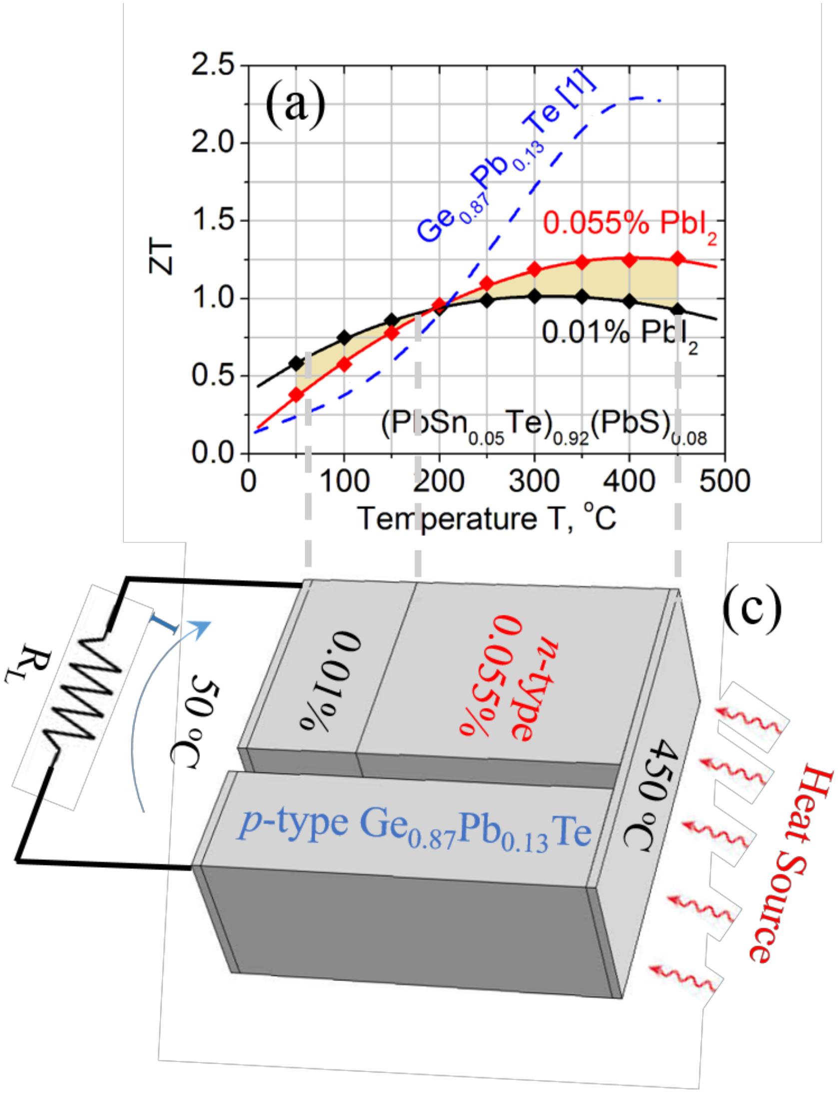


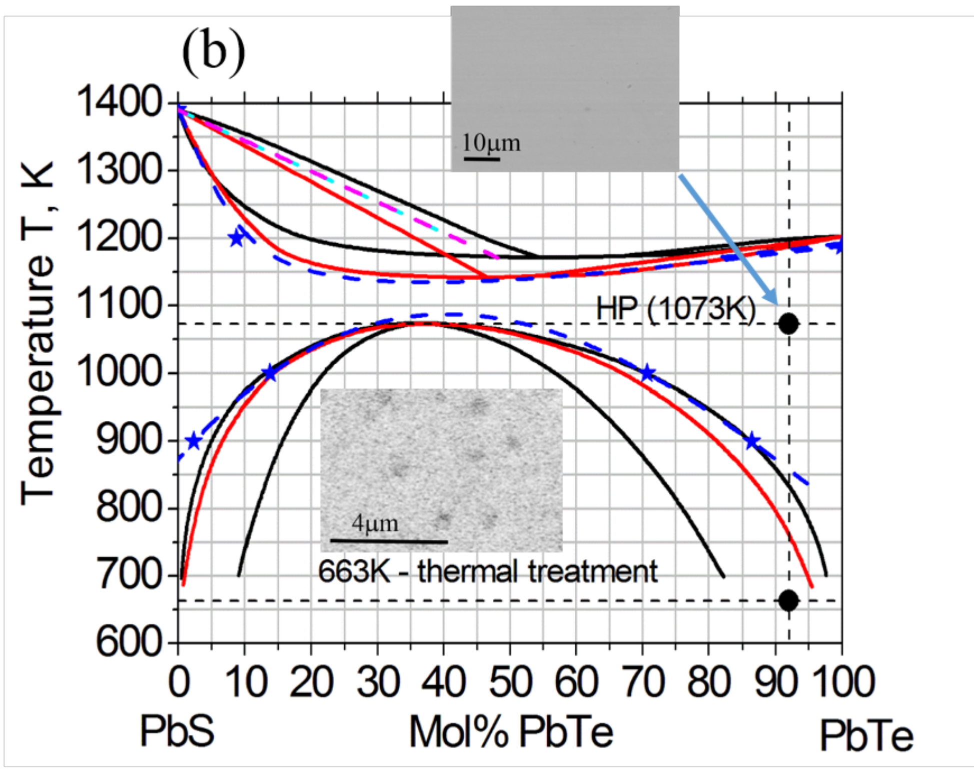
Spinodal Decomposition

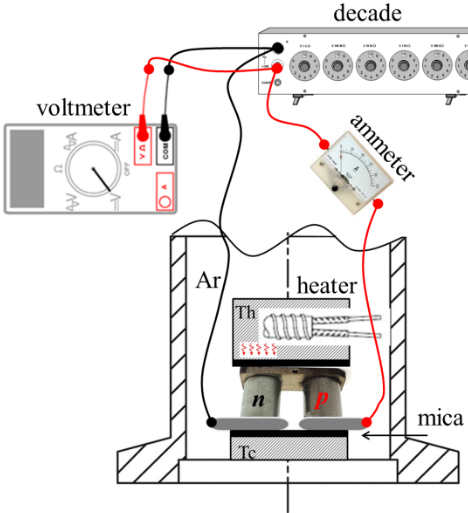
Nucleation & Growth

Physical Chemistry and Chemical Physics **16** 20120 (2014)

GePbTe-PbTe/PbS

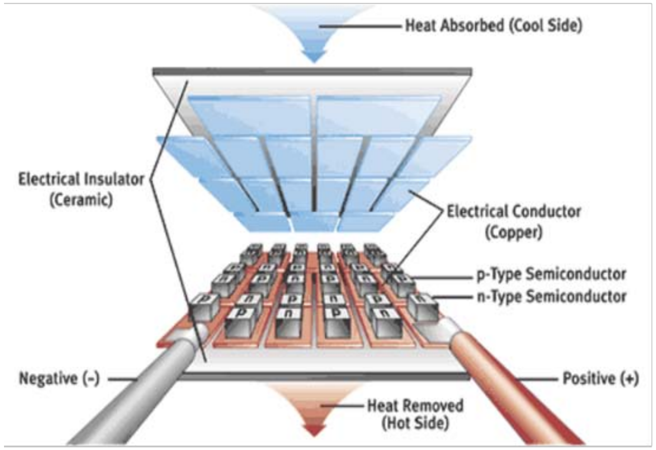




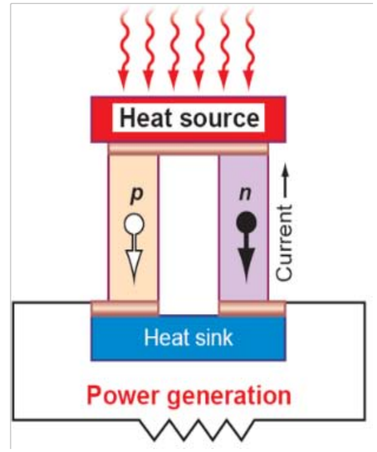


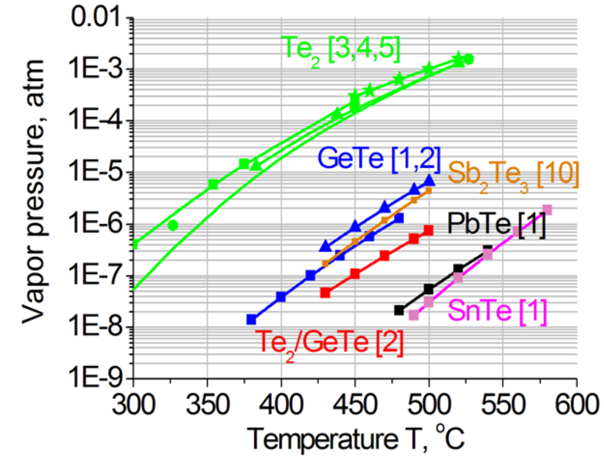
TRL increase – TE couples/devices challenges

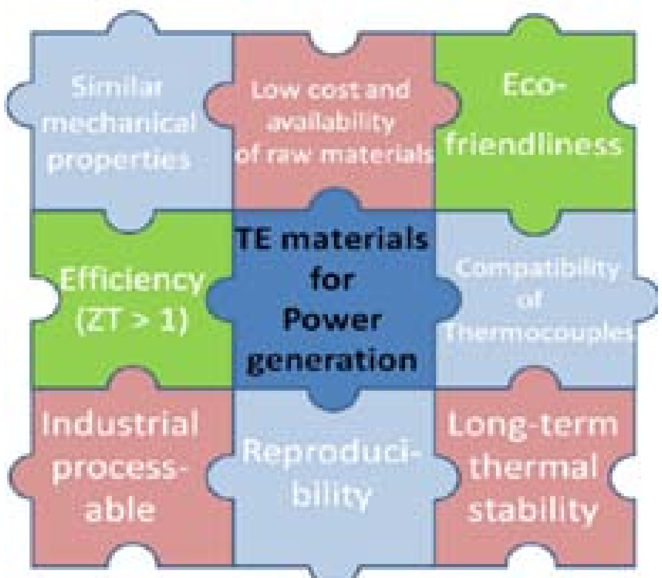
(a)

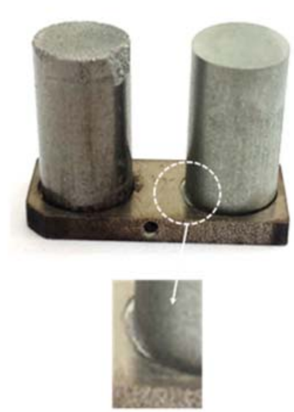


(b)

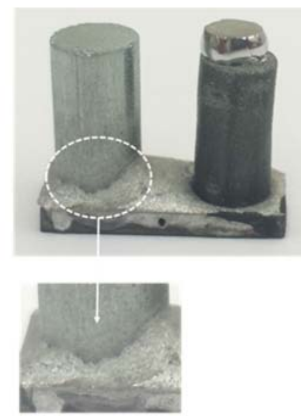








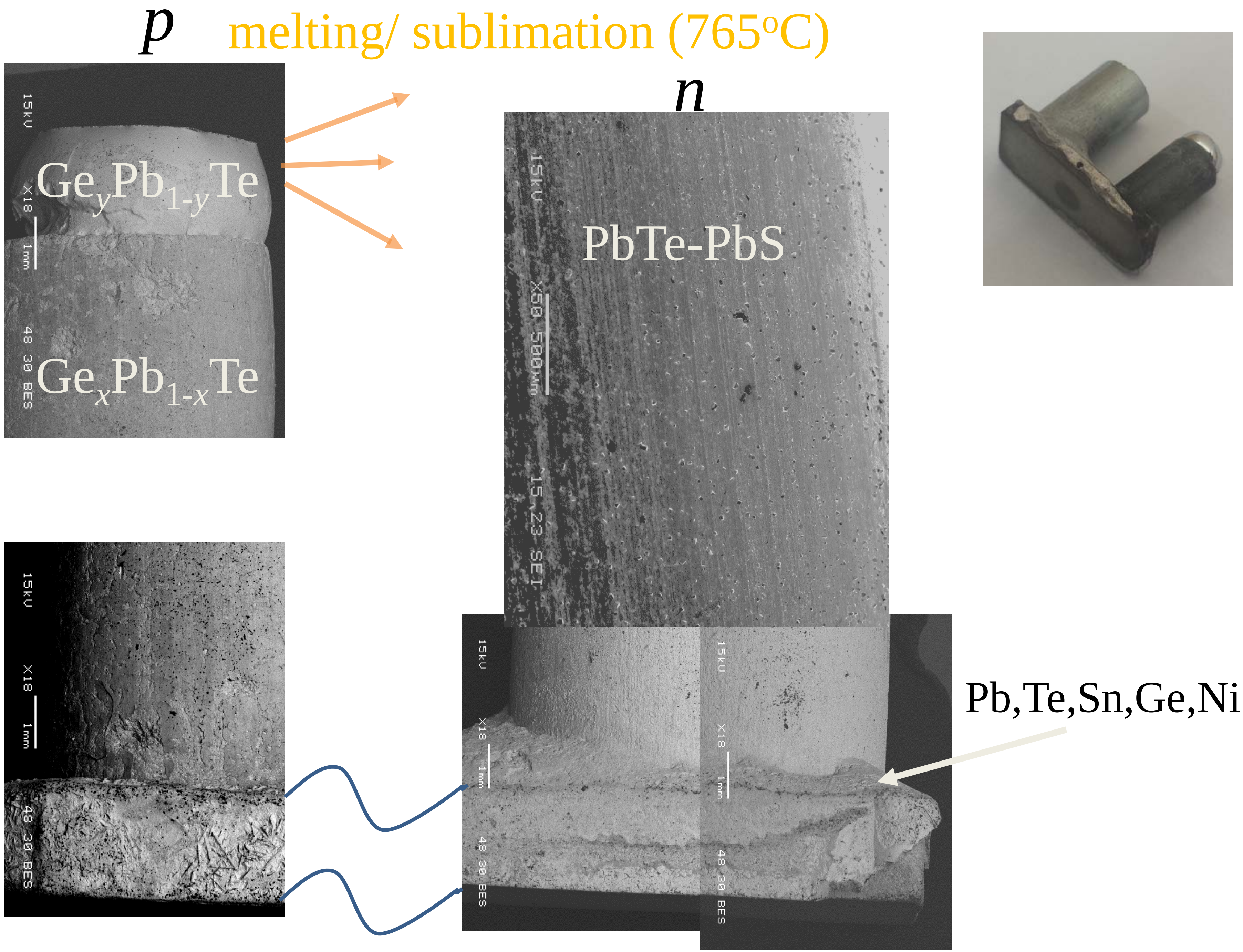
Fine brazing

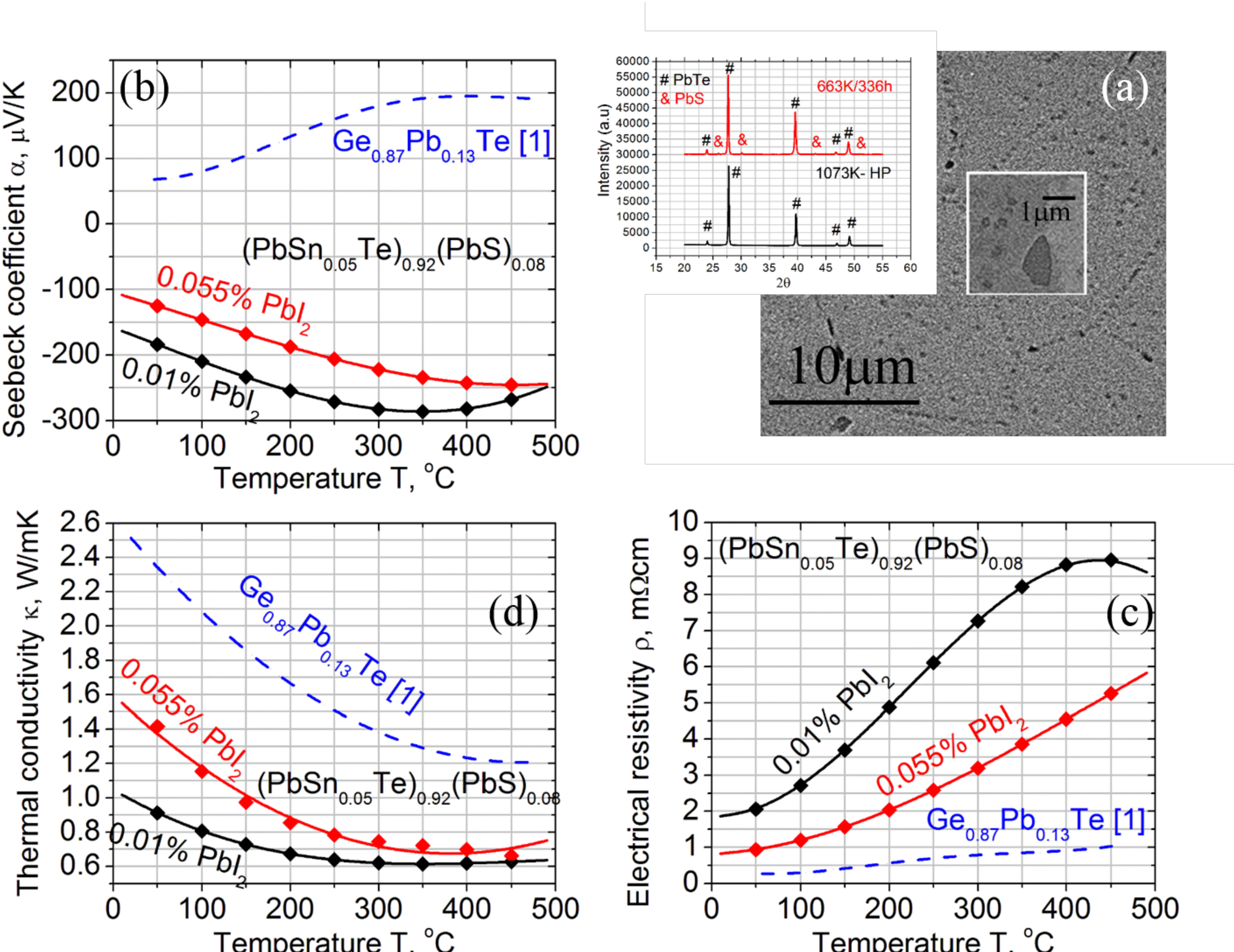


Sublimation products

Legs misalignment

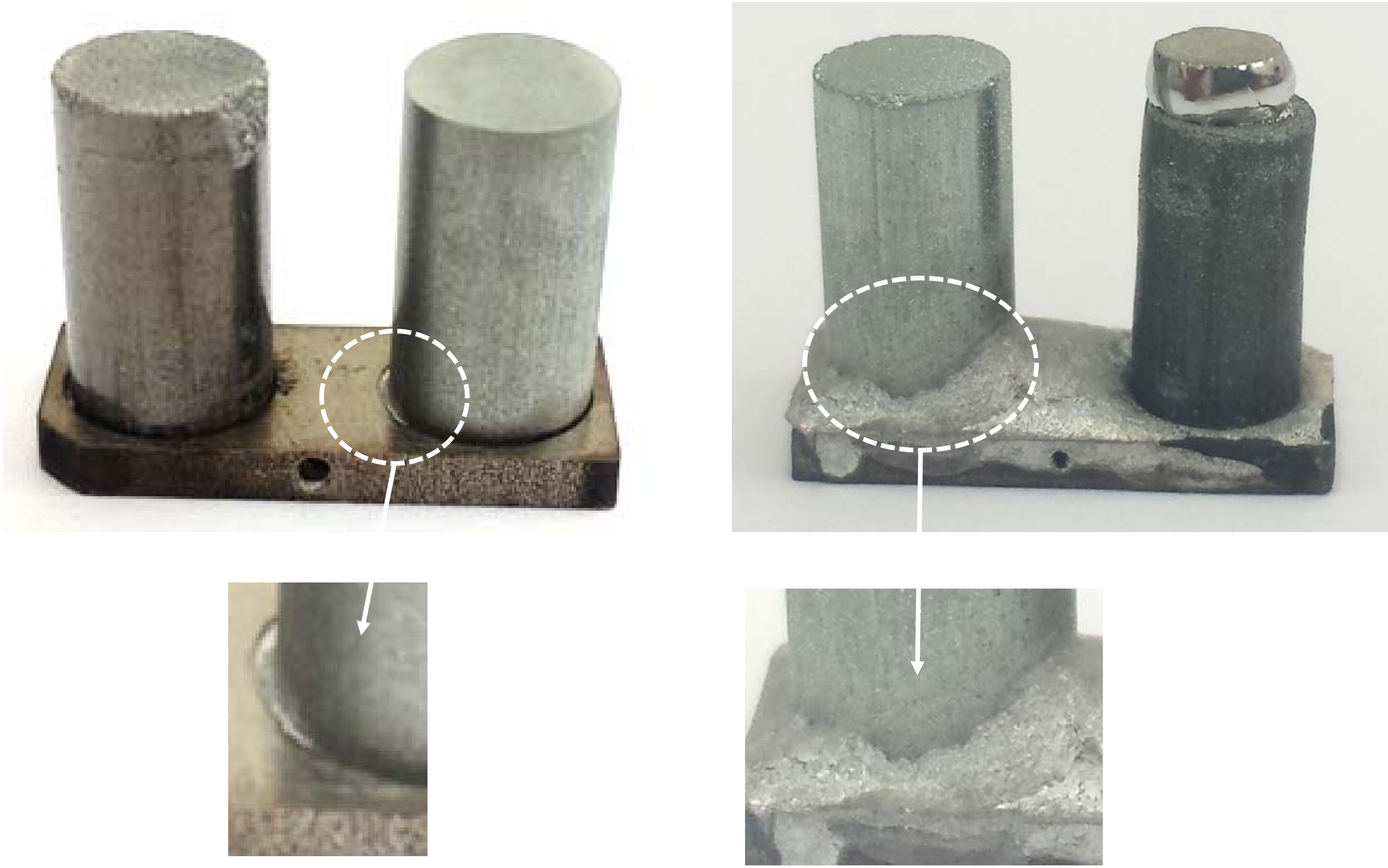
Brazing materials incompatibility - Reaction zone


p
melting/ sublimation (765ºC)
n
$Ge_yPb_{1-y}Te$
$Ge_xPb_{1-x}Te$
PbTe-PbS
Pb,Te,Sn,Ge,Ni

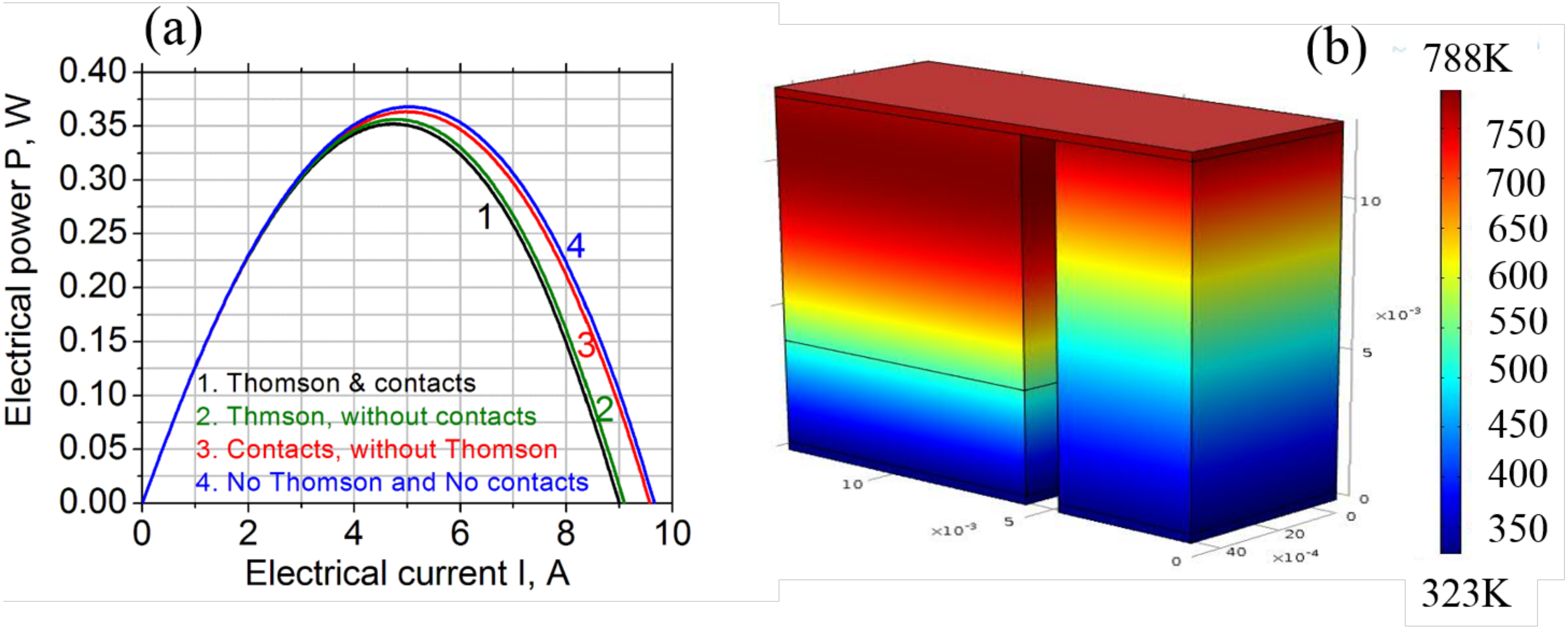


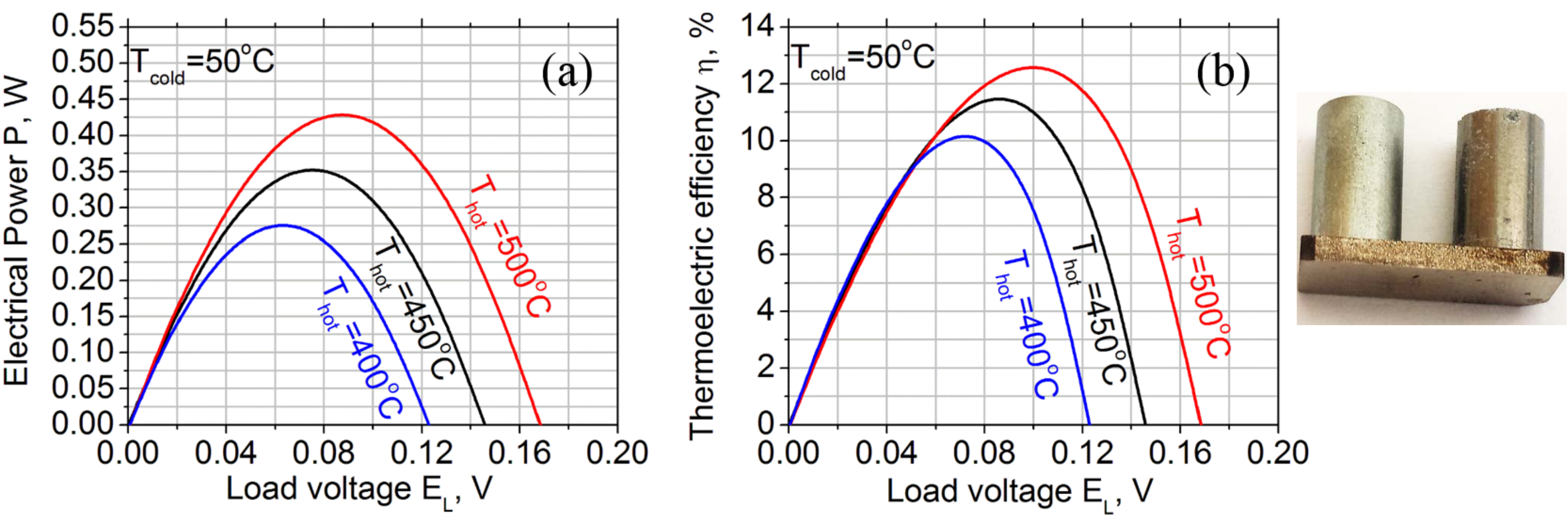
(b)
Seebeck coefficient α, μV/K
Ge0.87Pb0.13Te [1]
(PbSn0.05Te)0.92(PbS)0.08
0.055% PbI2
0.01% PbI2
Temperature T, °C
(a)
PbTe
& PbS
663K/336h
1073K- HP
Intensity (a.u)
2θ
1μm
10μm
(d)
Thermal conductivity κ, W/mK
Ge0.87Pb0.13Te [1]
0.055% PbI2
(PbSn0.05Te)0.92(PbS)0.08
0.01% PbI2
Temperature T, °C
(c)
Electrical resistivity ρ, mΩcm
(PbSn0.05Te)0.92(PbS)0.08
0.01% PbI2
0.055% PbI2
Ge0.87Pb0.13Te [1]
Temperature T, °C

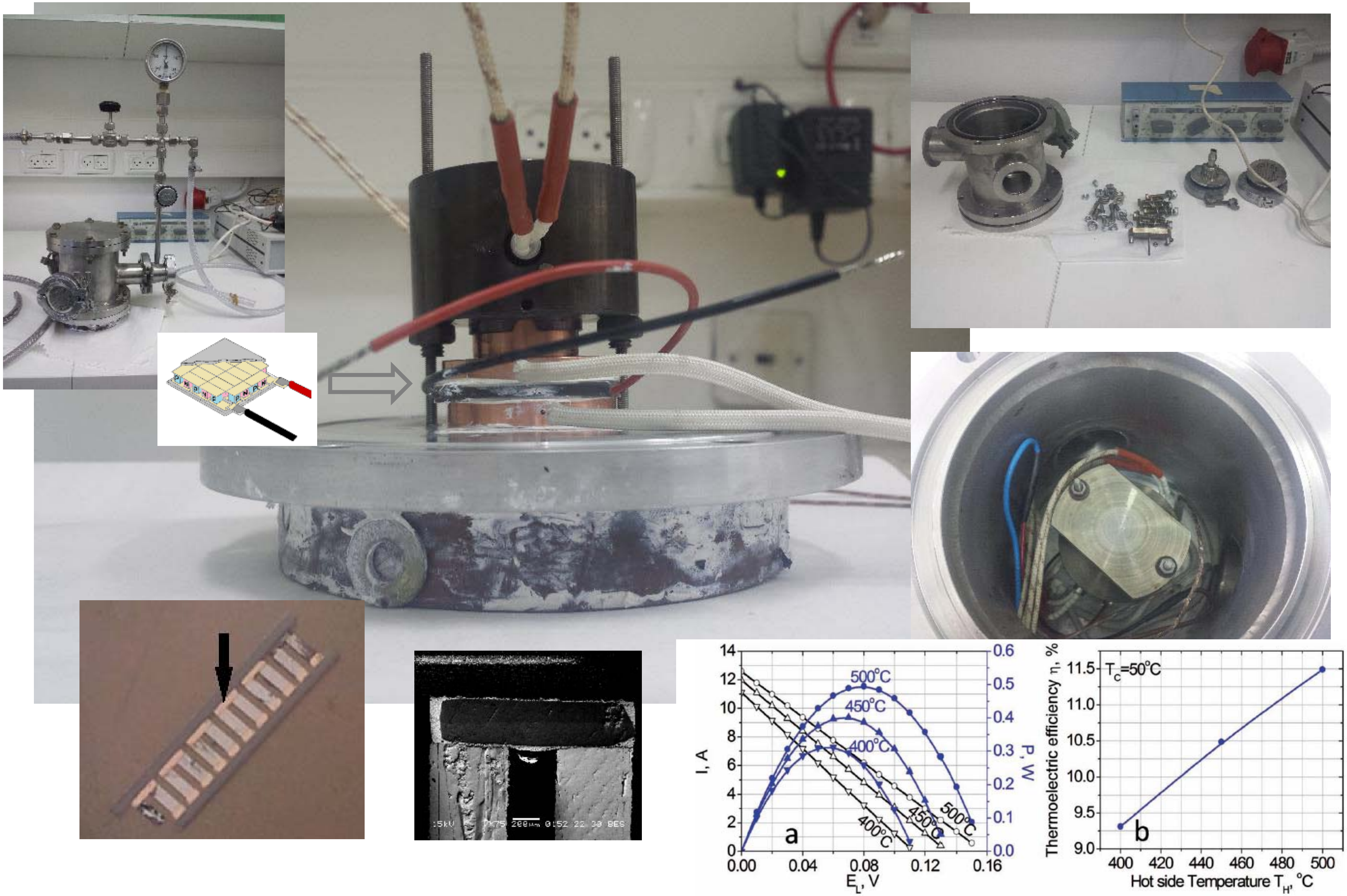
370°C 765°C



Soldering Soldering & Sublimation

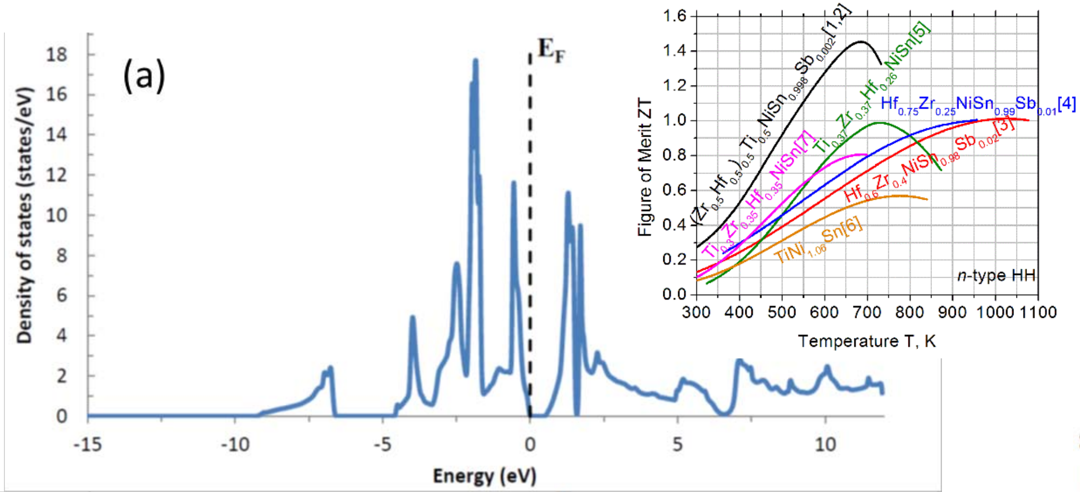

(a)
Electrical power P, W
Electrical current I, A
1
2
3
4
1. Thomson & contacts
2. Thmson, without contacts
3. Contacts, without Thomson
4. No Thomson and No contacts
(b)
788K
323K
750
700
650
600
550
500
450
400
350

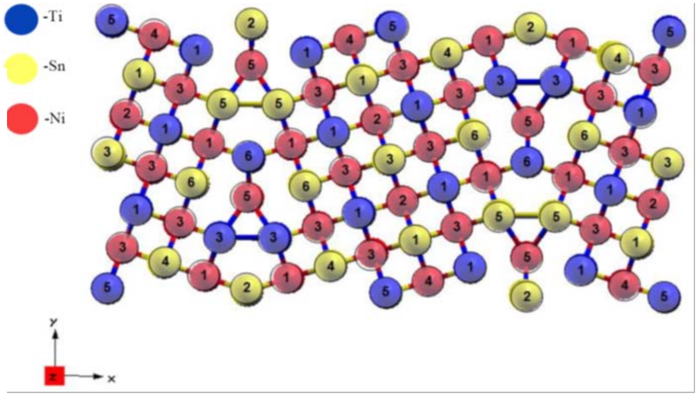

(a)
T_{cold}=50°C
Electrical Power P, W
Load voltage E_L, V
T_{hot}=500°C
T_{hot}=450°C
T_{hot}=400°C
(b)
T_{cold}=50°C
Thermoelectric efficiency η, %
Load voltage E_L, V
T_{hot}=500°C
T_{hot}=450°C
T_{hot}=400°C

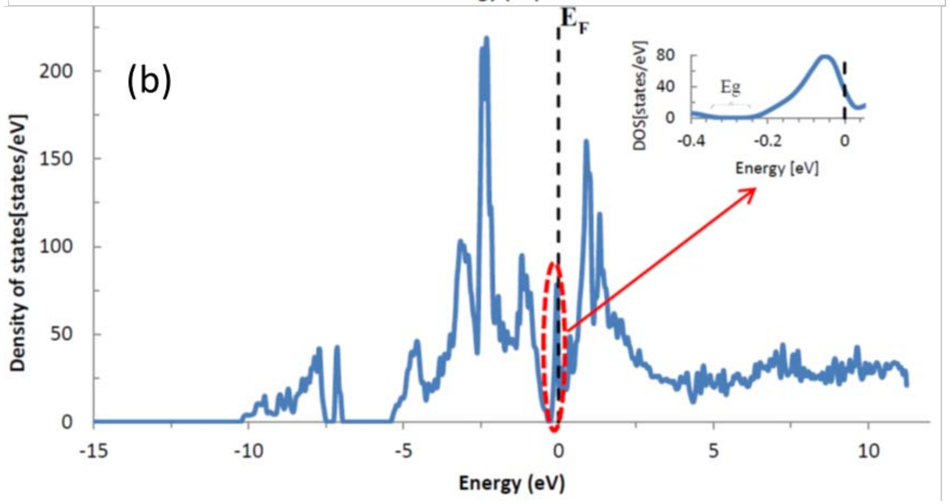


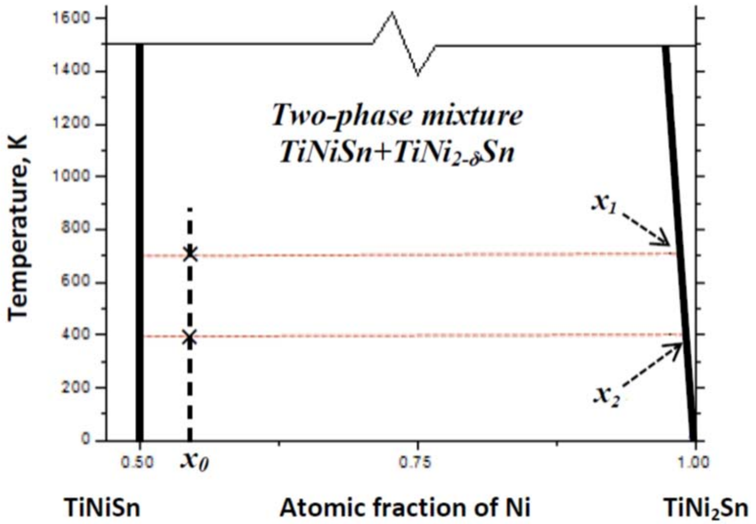
I, A
P, W
E_L, V
500°C
450°C
400°C
a
Thermoelectric efficiency η, %
T_C=50°C
Hot side Temperature T_H, °C
b

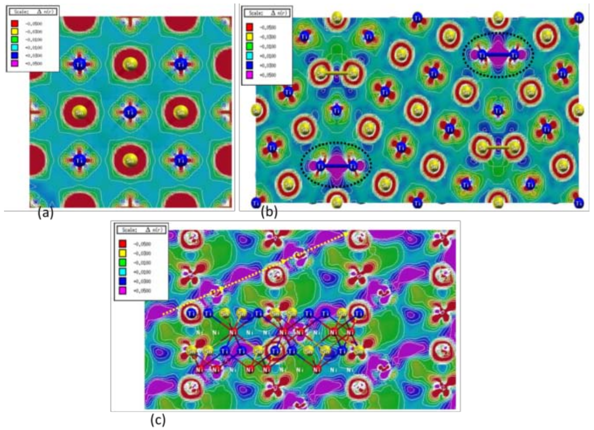
TiNiSn based half-Heuslers











Journal of Materials Research **26**(15) 1919-1924 (2011)

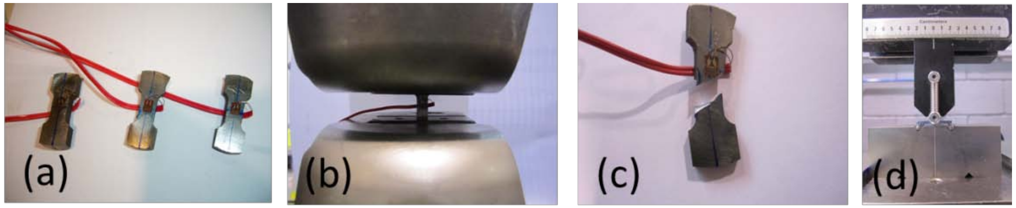
Journal of Electronic Materials **42**(7) 1340-1345 (2013)

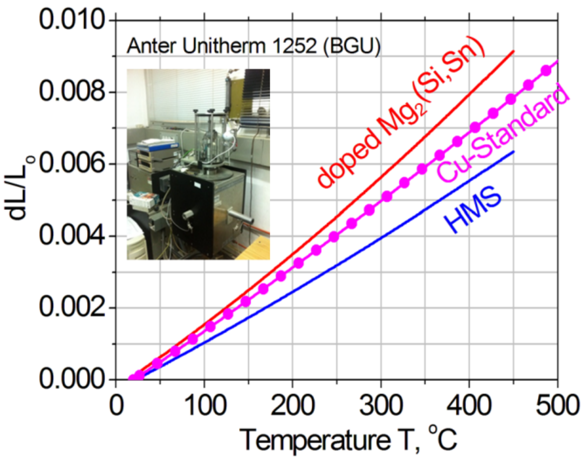
Journal of Solid State Chemistry **203** 247-254 (2013)

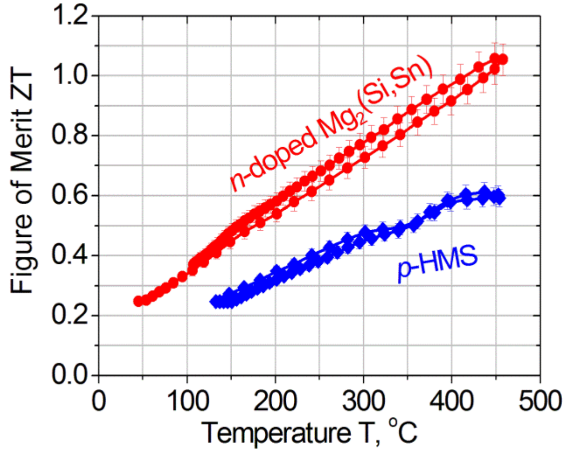
Journal of Electronic Materials **43**(6) 1976-1982 (2014)

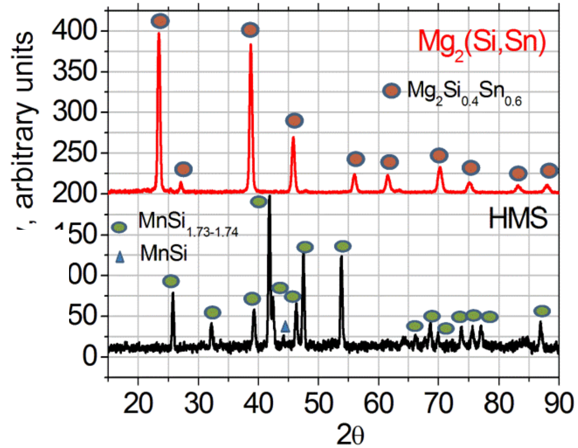
Physical Chemistry and Chemical Physics **16** 20023 (2014)

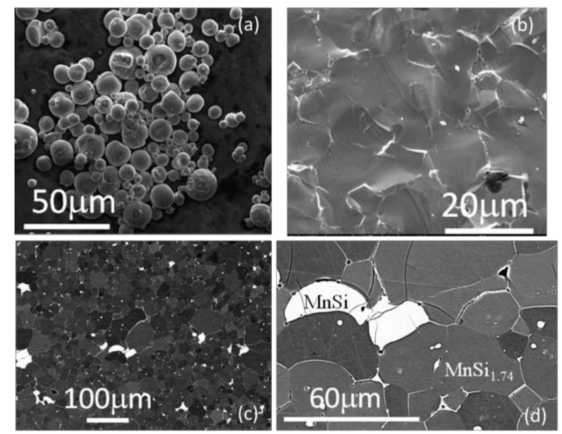
Silicides

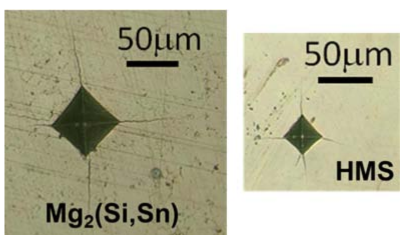


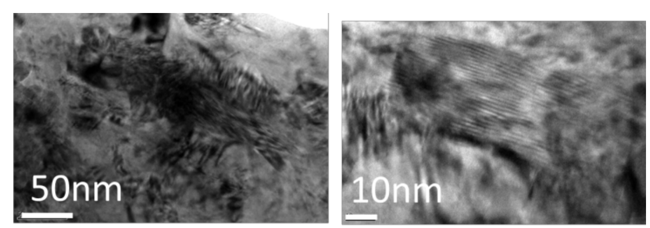






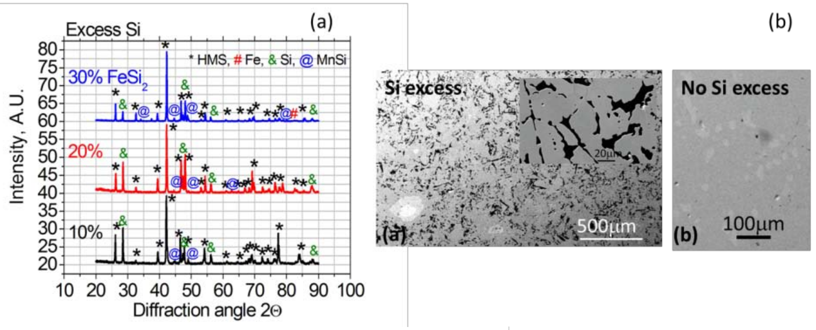


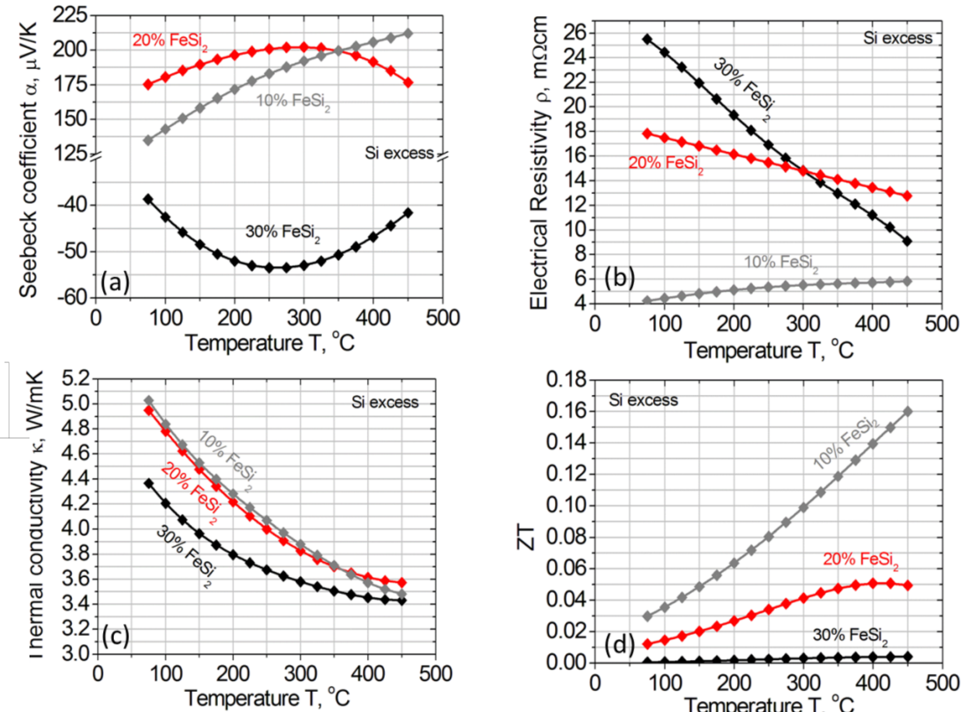


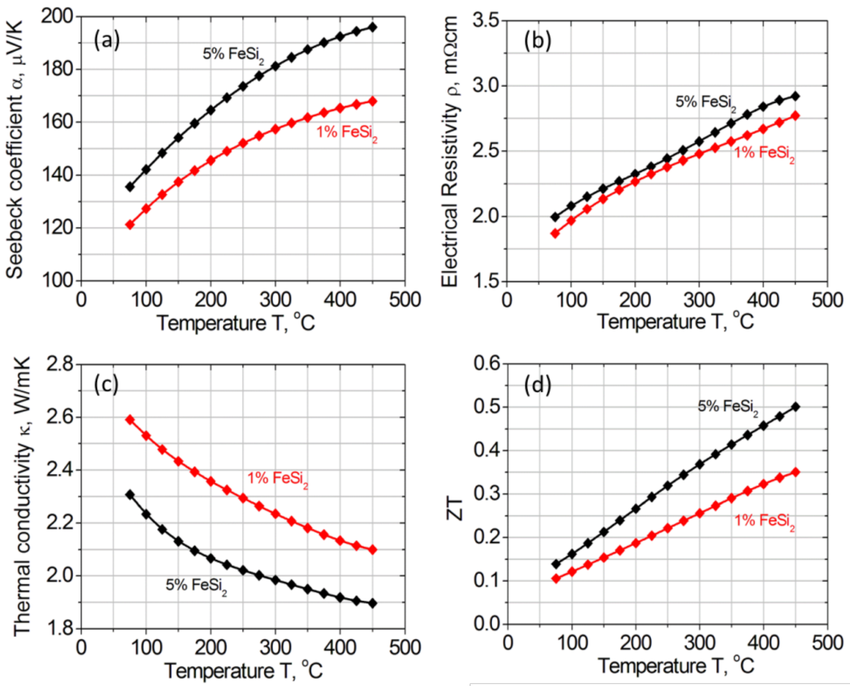


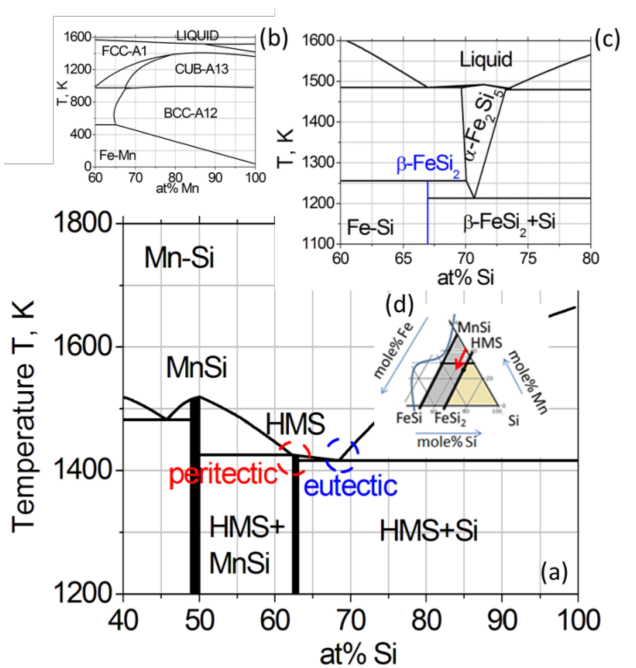
Journal of Electronic Materials **41**(6) 1504-1508 (2012)
Journal of Electronic Materials **42**(7) 1926-1931 (2013)
Journal of Nanomaterials **701268** (2013)
Journal of Electronic Materials **43**(6) 1703-1711 (2014)

Silicides



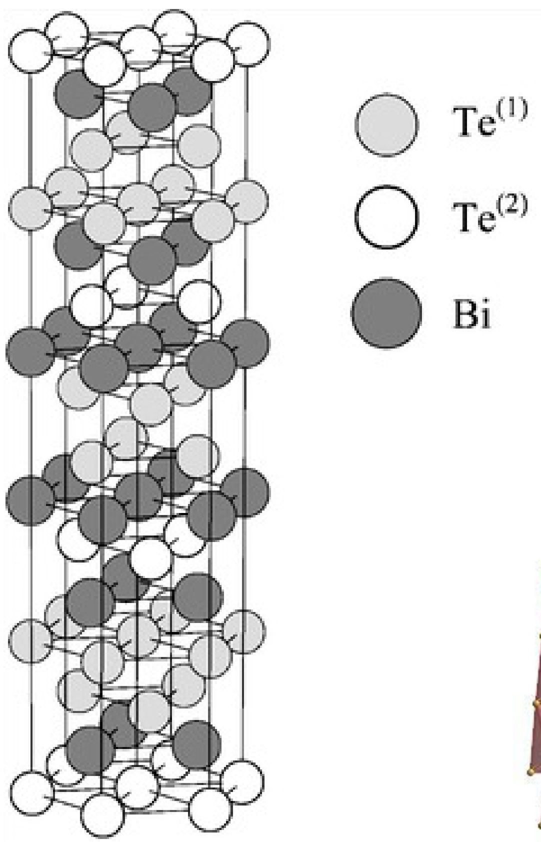


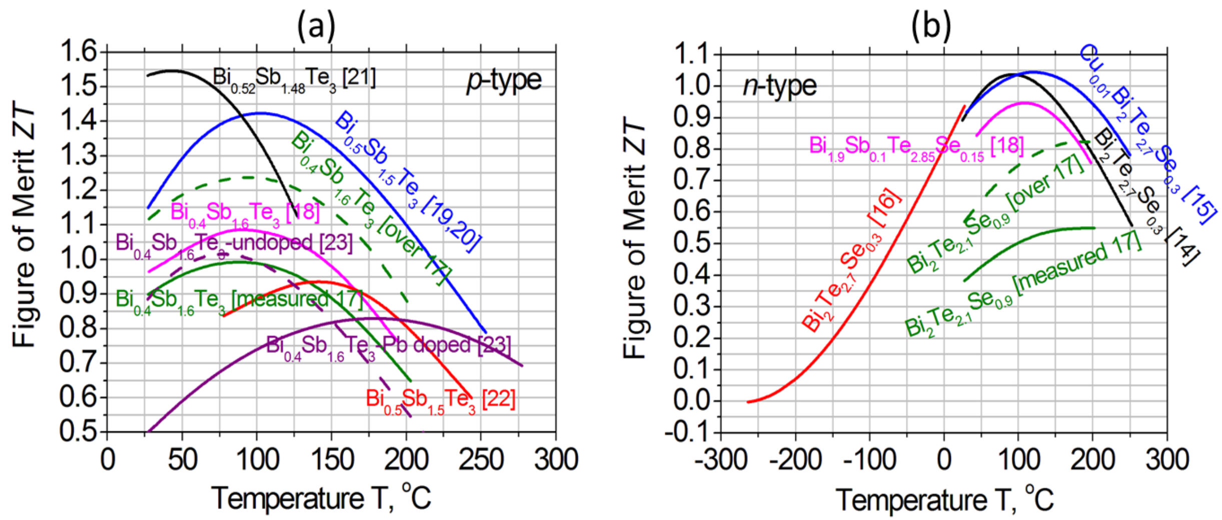


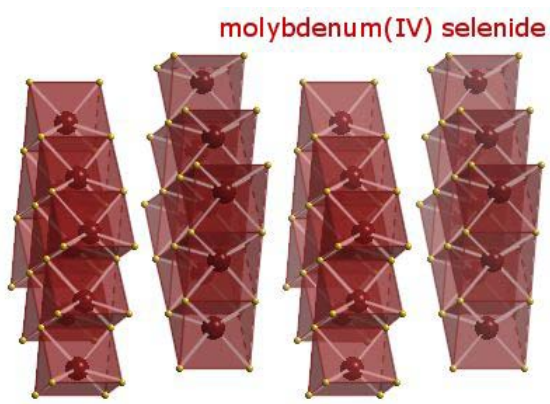


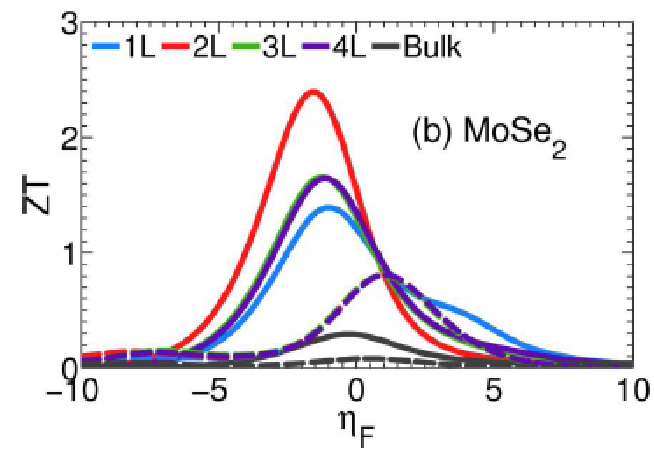
Journal of Electronic Materials **41**(6) 1504-1508 (2012)
Journal of Electronic Materials **42**(7) 1926-1931 (2013)
Journal of Nanomaterials **701268** (2013)
Journal of Electronic Materials **43**(6) 1703-1711 (2014)

Bi_2Te_3 based materials





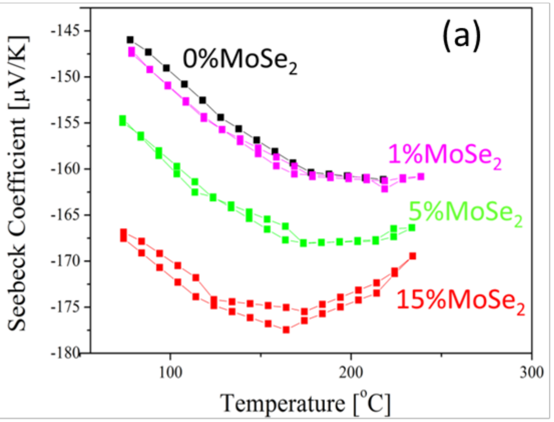


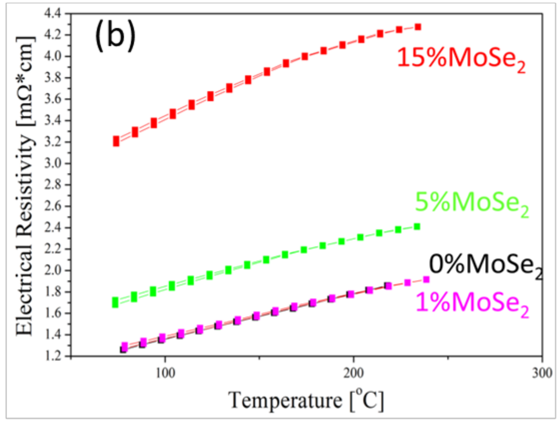


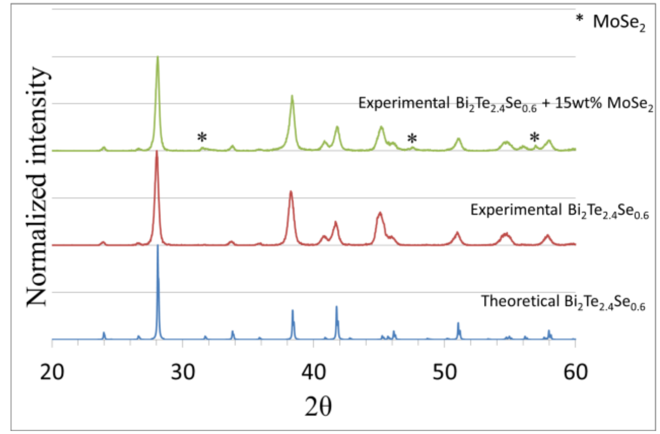
Wickramaratne, Zahid and Lake, *arXiv:1401.0502v2* (2014)

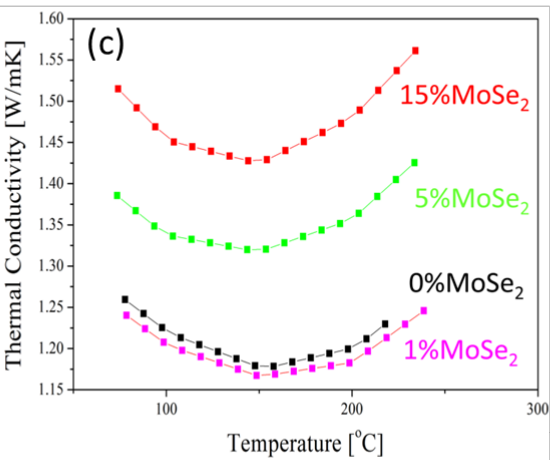
Journal of Applied Physics **101**, 113707 (2007)

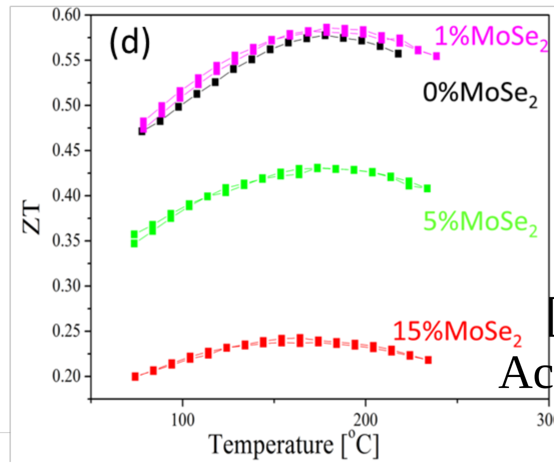
Journal of Electronic Materials **41**(6), 1546-1553 (2012)

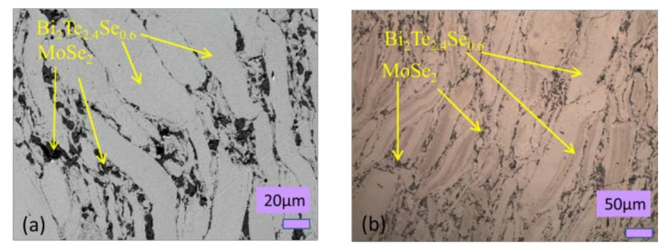








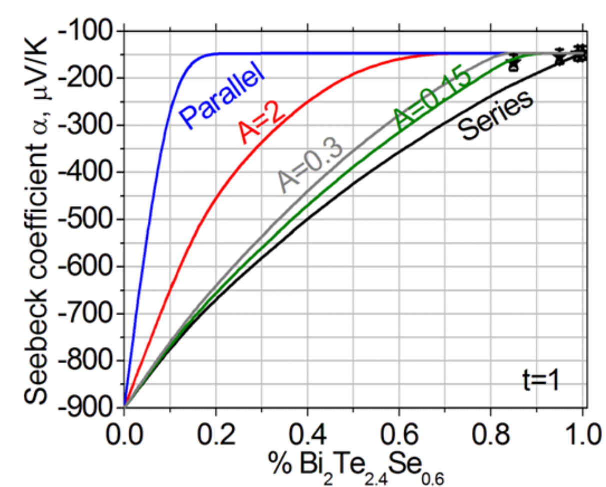


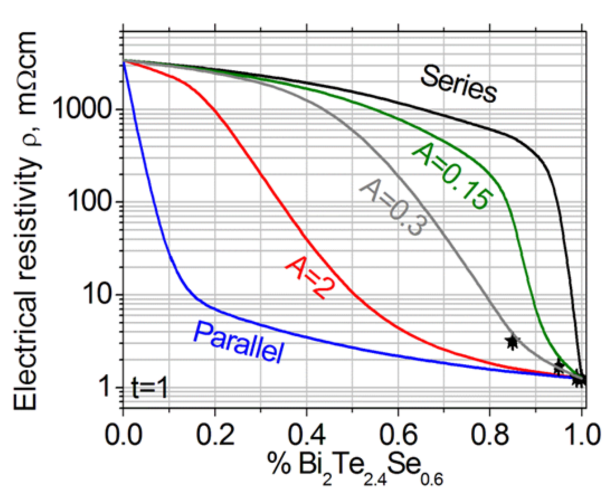


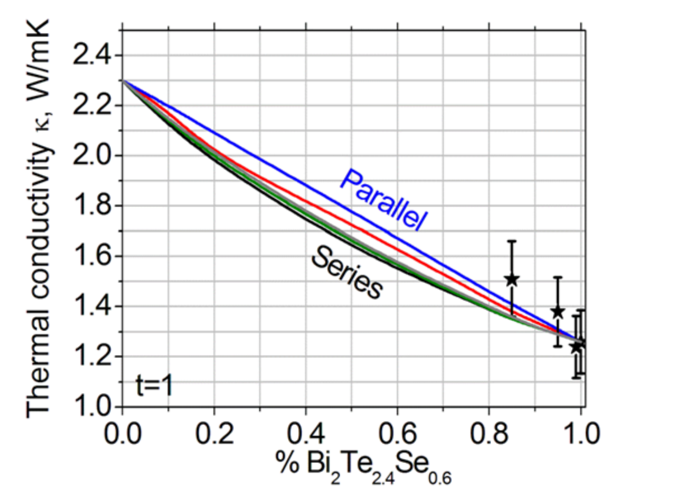
$[Bi_2Te_{2.4}Se_{0.6}(0.1wt\%CHI_3)]_x[MoSe_2]_{1-x}$

Accepted: DOI:10.1007/S11664-014-3381-1

(c)







Conclusions-

- Many classes of thermoelectric materials are being investigated at BGU for various power generation applications including automotive, marine and PV-TE.

- Both high efficiency and nano-structures stability under practical applications conditions are considered.

- Both experimental and theoretical approaches are being applied for achieving the group’s agenda.

- Advanced methods for nano-structuring of bulk thermoelectric materials including thermodynamic / physical metallurgy driven nano-features methods are investigated.

- High maximal thermoelectric figure of merit (*ZT*) values of >2 were obtained so far with reasonable stability characteristics, putting the materials developed in the group at the first line of the most advanced thermoelectric materials developed so far globe wide.

- Couples and devices results are on the way.

Research Staff & Collaborators

- Research Staff
  - Prof. Moshe Dariel, Prof. Nahum Frage, Prof. David Fuks, Mr. Joseph Marciano, Mr. Yair George, Dr. Vladimir Kasiyan, Dr. Ofer Beeri.

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- Collaborators
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  - Prof. Mercouri Kanatzidis, Northwestern University.
  - Prof. Ctirad Uher, UM.
  - Prof. Theodora Kyratsi, University of Cyprus.
  - Prof. Claudia Felser & Dr. Benjamin Balke, Uni-Mainz.
  - Mr. Martin Köhne, Bosch GmbH.
  - FP7 "*Power-Driver*" team.
  - Mr. Ricardo Albeida, Vossloh, Valencia.

Thanks for your attention.