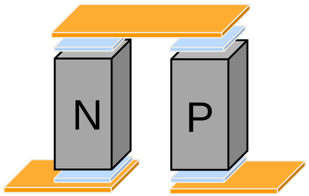
UK Thermoelectric Network Meeting
Herriot Watt University, Edinburgh
13th February 2018

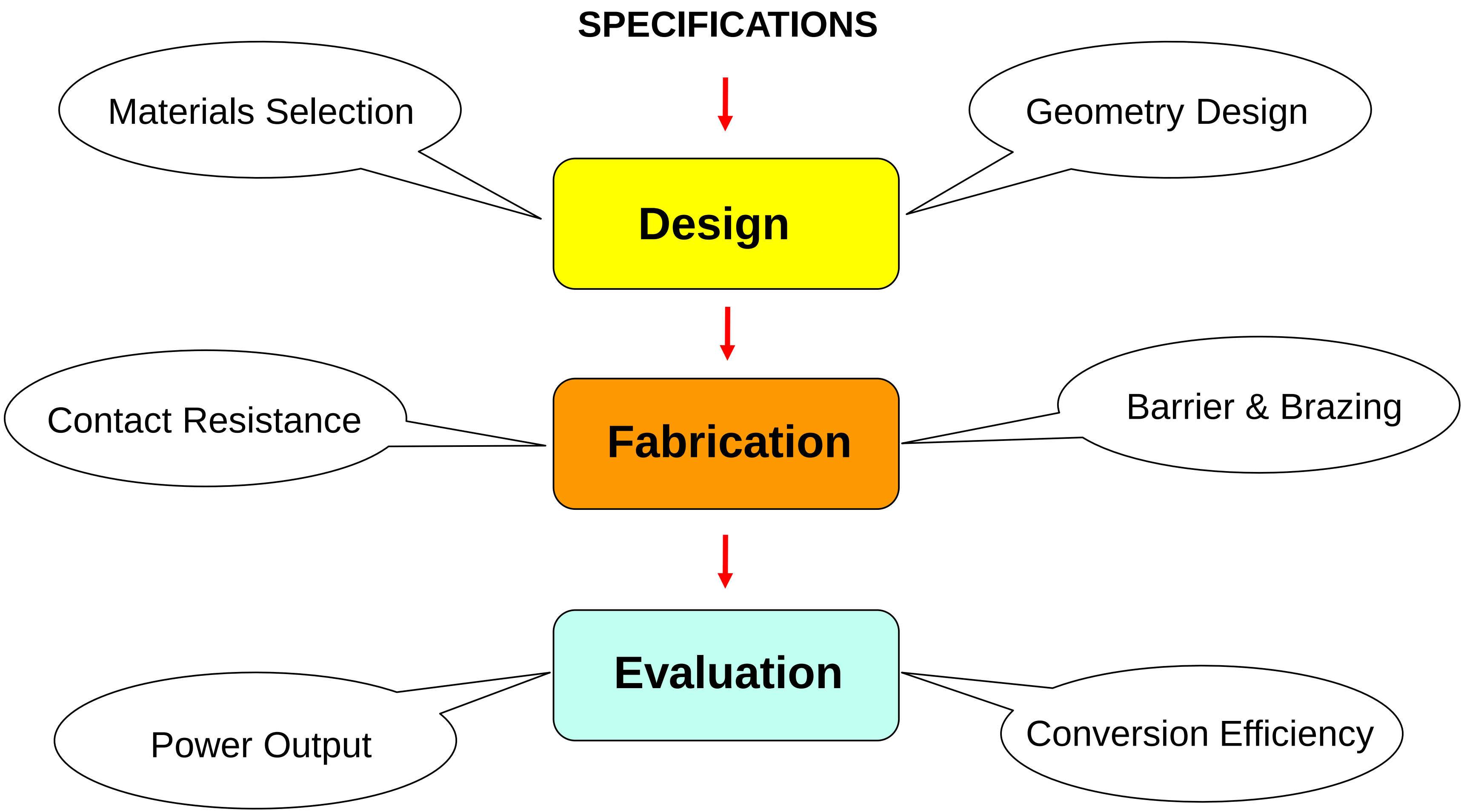
Key Issues in Design and Fabrication of Thermoelectric Modules



Gao Min

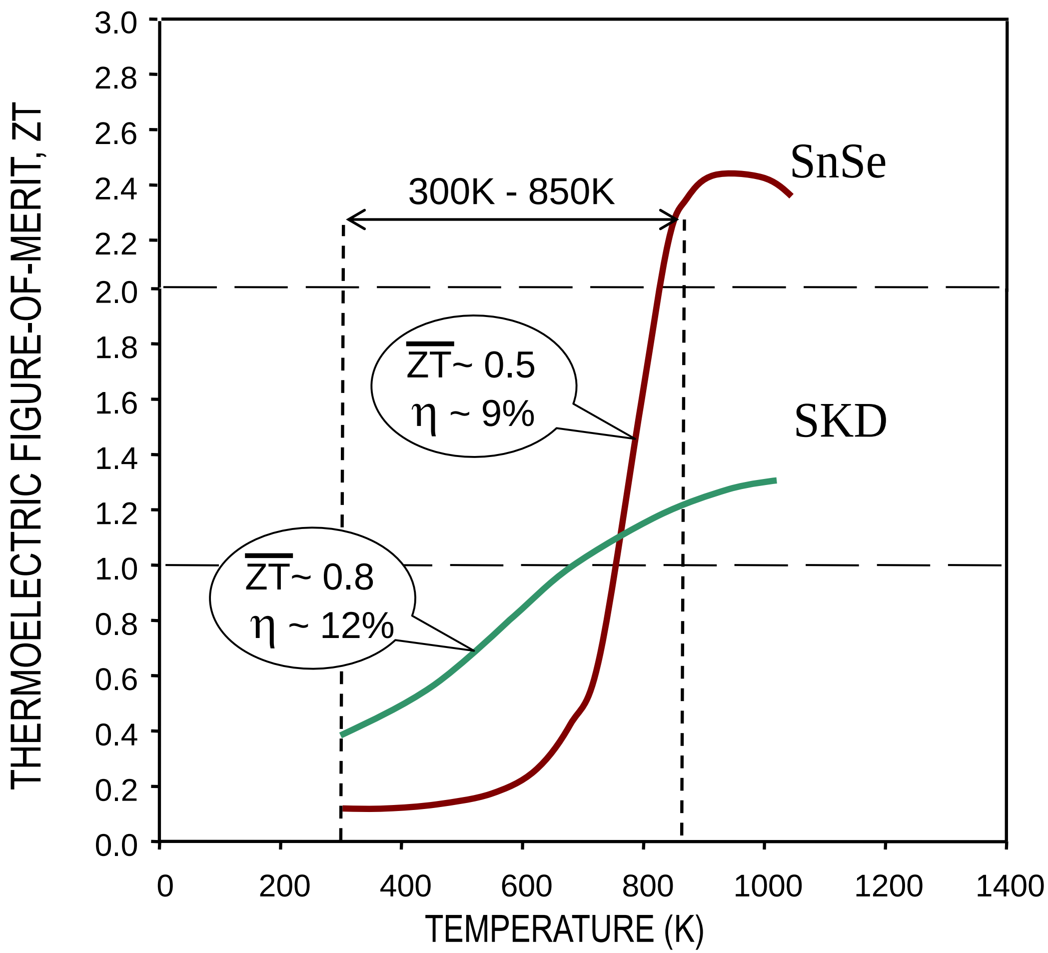
School of Engineering, Cardiff University

Design and Fabrication Processes



Selection of Thermoelectric Materials

- **Large average ZT**
- **Matching N and P**
  (e.g. SKD vs Silicide)
- **Manufacturability**
  (e.g. Half-heusler vs SKD)
- **Thermal stability**
  (e.g. Half-heusler vs SKD)
- **Non-toxicity**
  (e.g. Silicide vs PbTe)
- **Abundances**
  (e.g. Silicide vs Bi_2Te_3)



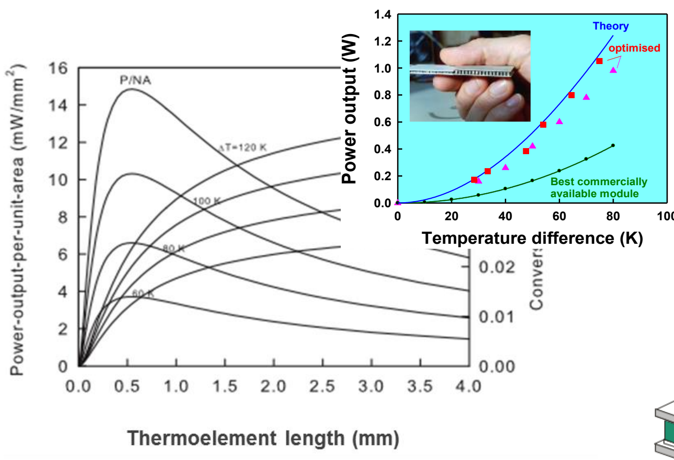
Design of Thermoelement Geometry

Nature of Heat Source

Constant ΔT

$$P_{\max} = \frac{(\alpha \cdot \Delta T)^2}{4\rho} \frac{A \cdot 2N}{(n+l)(1+2rl_c/l)^2}$$

$$\phi = \frac{\left(\frac{\Delta T}{T_H}\right)}{\left(1+2r\frac{l_c}{l}\right)^2\left(2 - \frac{1}{2}\left[\frac{\Delta T}{T_H}\right] + \left[\frac{4}{ZT_H}\right]\left[\frac{l+n}{l+2rl_c}\right]\right)}$$

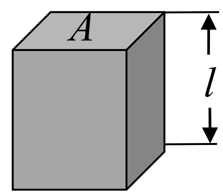


Shorter legs (down to ~500μm)

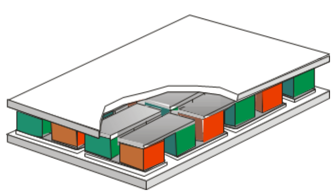
Constant heat flux

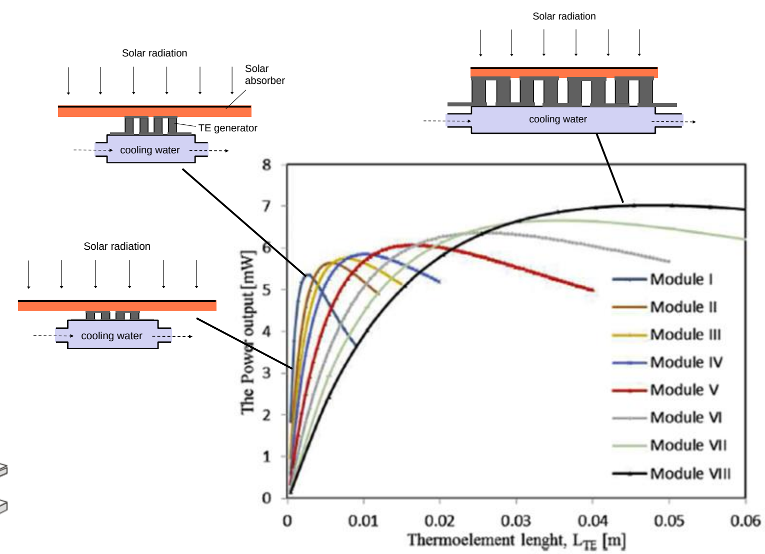
$$P = \frac{s}{(1+s)^2} \times \frac{Z}{(1+ZT_M)^2} \times \frac{\dot{Q}^2}{\lambda} \times \frac{l}{A} \times \frac{l}{(n+l)(1+2rl_c/l)^2}$$

$$\phi = \frac{P}{\dot{Q}} = \frac{s}{(1+s)^2} \times \frac{Z}{(1+ZT_M)^2} \times \frac{\dot{Q}}{\lambda} \times \frac{l}{A} \times \frac{l}{(n+l)(1+2rl_c/l)^2}$$



$A/l = ?$

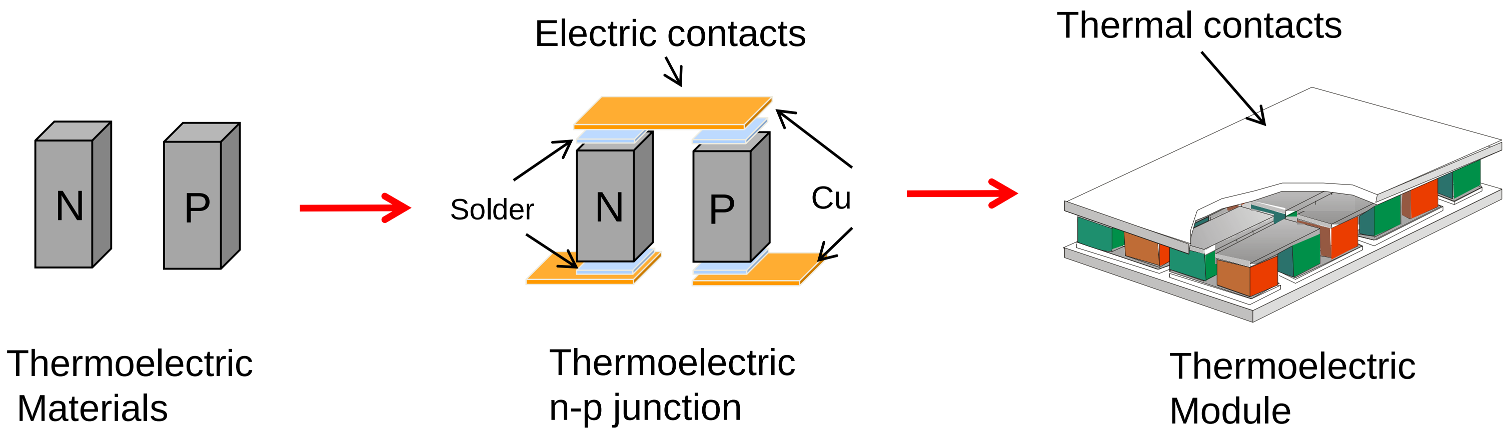




Longer legs (typically 3-8 mm)

G Min and Rowe, 2002, Energy Conversion & Management , (43) 221-228
G Min, CRC Handbook of Thermoelectrics, 1996, 11-1
G Min, "TE Design for a Given Thermal Input" J.Electr. Mater. (2013), 42(7), 2239-2242.
H Hashim, JJ Bomphrey, G Min, Renewable Energy, 87(2016), 458-463

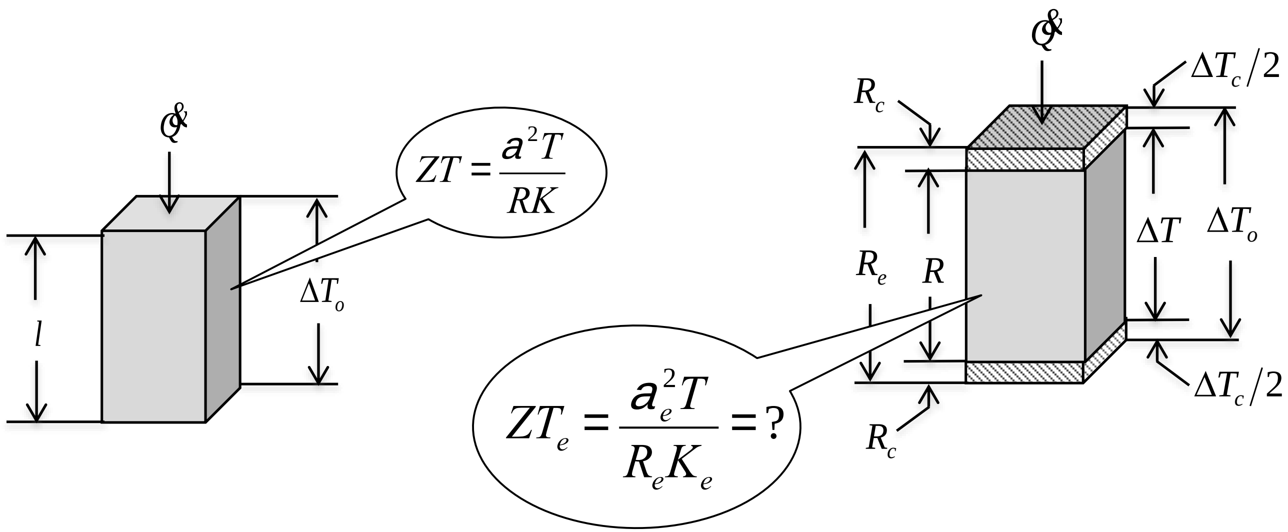
Materials to Module – Interfaces Challenge



Role: To join and hold the N- and P-type thermoelements together.

Requirements:
- Mechanical strength.
- Temperature stability and durability.
- No reduction in thermoelectric properties.

Influence of Contacts – Theoretical Consideration



Bulk properties:

$$R = \rho(l/A)$$

$$K = \lambda(A/l)$$

$$\frac{ZT_e}{ZT} = \frac{1}{(1+2\rho_c/\rho l)(1+2\lambda/\lambda_c l)}$$

$ZT_e < ZT$ due to ρ_c , λ_c

$$\alpha_e = \frac{\alpha}{1+2\lambda/\lambda_c l}$$

$$R_e = R\left(1+\frac{2\rho_c}{\rho l}\right)$$

$$K_e = \frac{K}{1+2\lambda/\lambda_c l}$$

Contact properties:

$$R_c = \rho_c/A$$

$$K_c = \lambda_c A$$

ZT will be reduced due to the interfaces. The degree of reduction depends on contact properties, materials properties, and leg length

G Min and M Phillips, 2016, "Preparation and Characterisation of TE Interface" Chapter 6 in Thermoelectric Energy Conversion (Eds. Pineda & Rezania, Wiley-Vch), 111-125

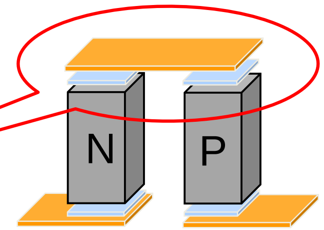
Manufacturing Requirements

Case study based on Bi_2Te_3: aims to limiting ZT reduction within 10%.

Assume:

- 5% due to ρ_c.
- 5% due to λ_c.
- $\rho = 10^3\ \Omega cm$.
- $\lambda = 1.5\ W/mK$.

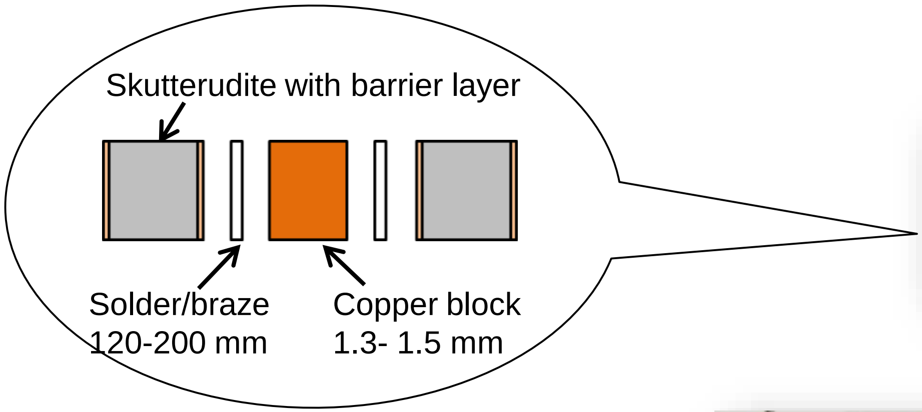
l (mm)	ρ_c (Ωcm^2)	k_c (W/m^{2}K)
0.1	2.6×10^{-7}	5.7×10^{5}
0.5	1.3×10^{-6}	1.1×10^{5}
1.0	2.6×10^{-6}	5.7×10^{4}
1.5	4.0×10^{-6}	3.8×10^{4}
2.0	5.3×10^{-6}	2.9×10^{4}
2.5	6.6×10^{-6}	2.3×10^{4}
3	7.9×10^{-6}	1.9×10^{4}
5	1.3×10^{-5}	1.1×10^{4}



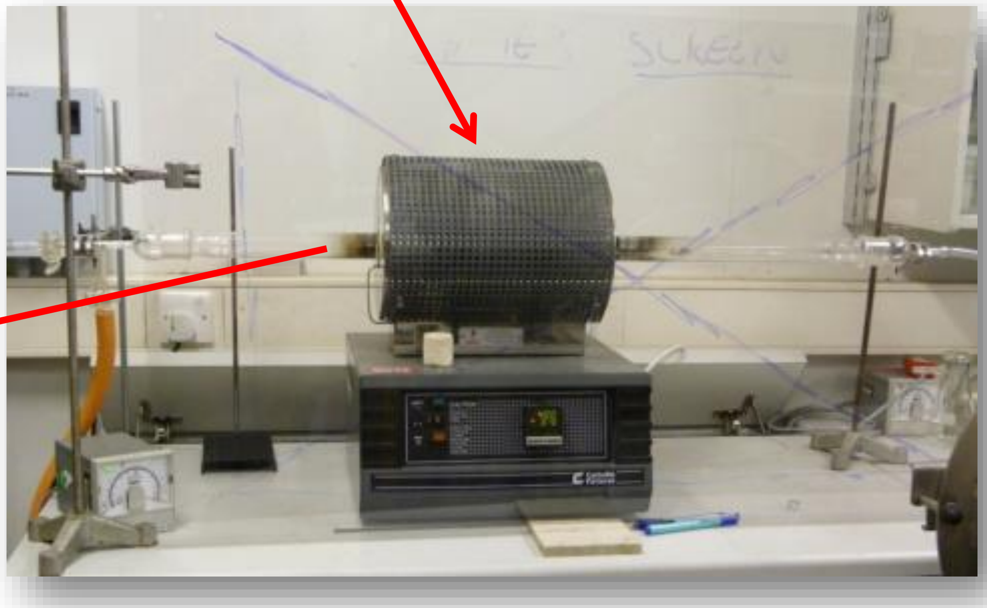
$$\frac{ZT_e}{ZT} = \frac{1}{(1+2\rho_c/\rho l)(1+2\lambda/\lambda_c l)} = 90\%$$

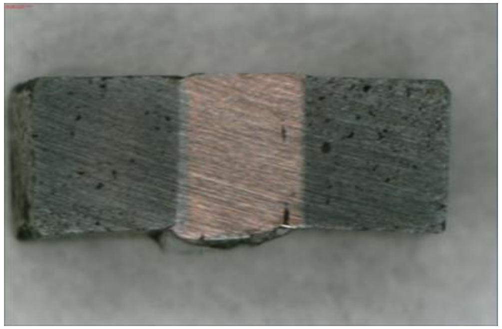
L = 2mm It requires: $\rho_c \sim 5\text{x}10^{-6}\ \Omega cm^2$ and $\lambda_c \sim 3\text{x}10^{4}\ W/m^2K$

Sample Preparation for Interface Studies



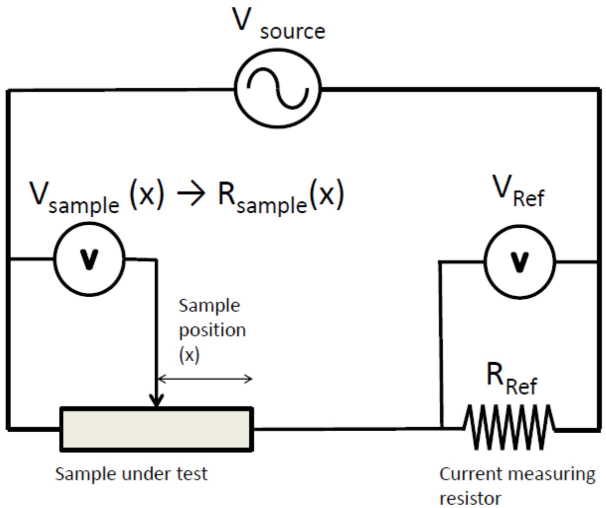
Brazing holder





Brazing (or soldering) in argon gas or vacuum

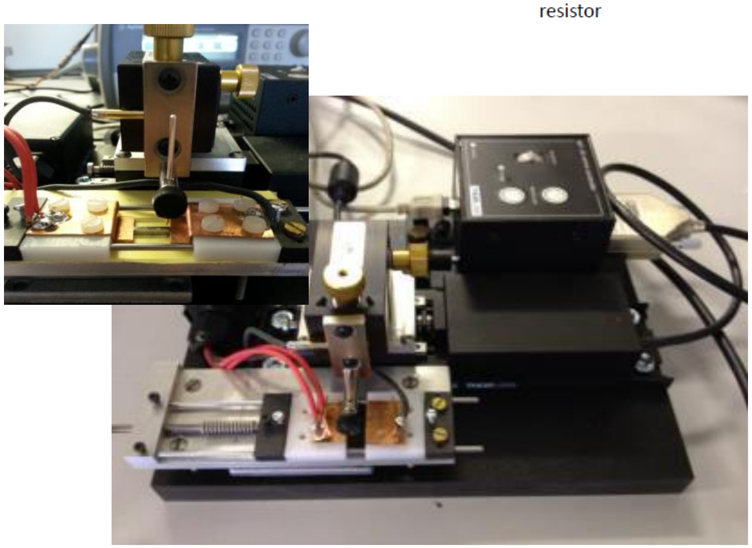
High-resolution Scanning Voltage Probe for Measuring Electrical Contact Resistance

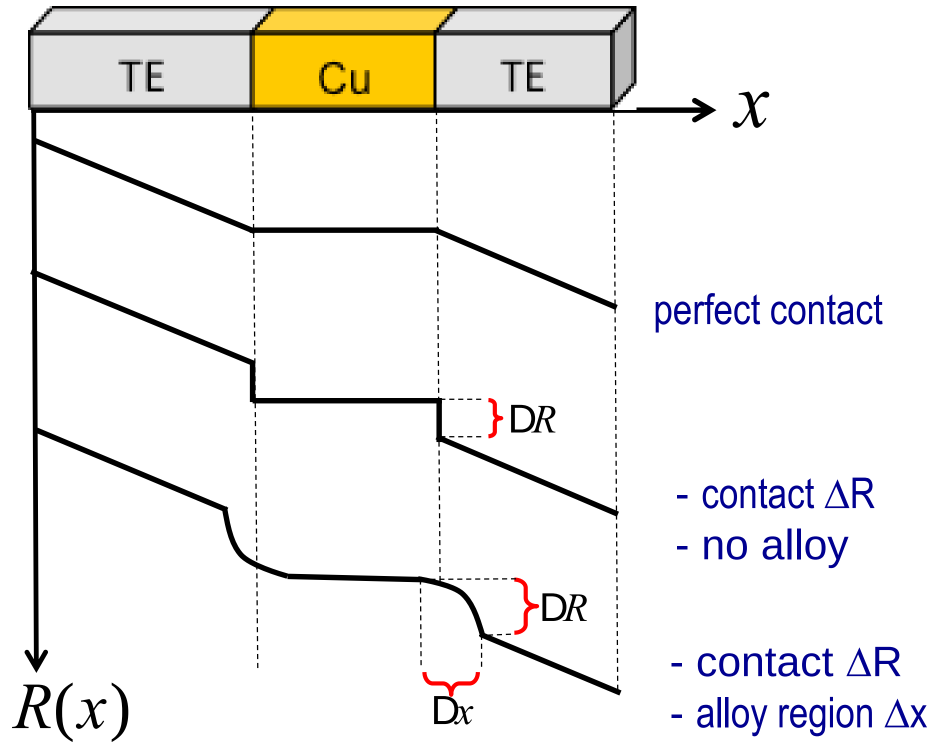


$$R(x) = \frac{V_S(x)}{V_{ref}} \times R_{ref}$$

$$r_c = \Delta R \cdot A$$

$$r = dR(x)/dx$$





High Resolution Scanning Voltage Probe (1 μm)

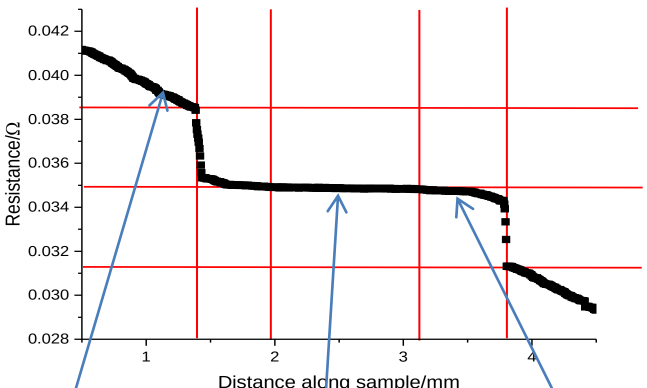
The key is appropriate spatial resolution (~1μm for for bulk modules)

G Min and M Phillips, 2016, "Preparation and Characterisation of TE Interface" Chapter 6 in Thermoelectric Energy Conversion (Eds. Pineda & Rezania, Wiley-Vch), 111-125

Characterisation of Skutterudite Interfaces

SVP Measurement

Pd/Cu/$Ag_{50}Cu_{20}Zn_{28}Ni_2$



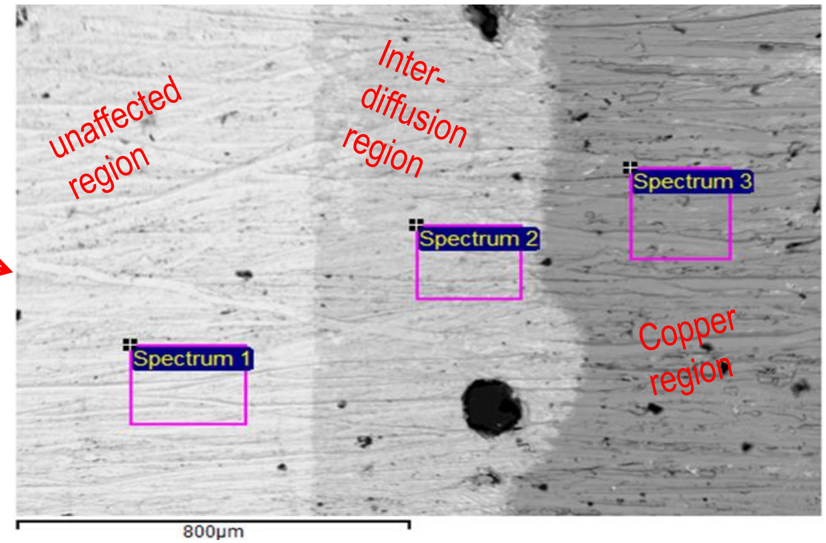
Unaffected region

Copper region

Inter-diffusion region

High resolution scanning voltage probe measurement indicates the formation of alloying region.

SEM and EDX Analysis



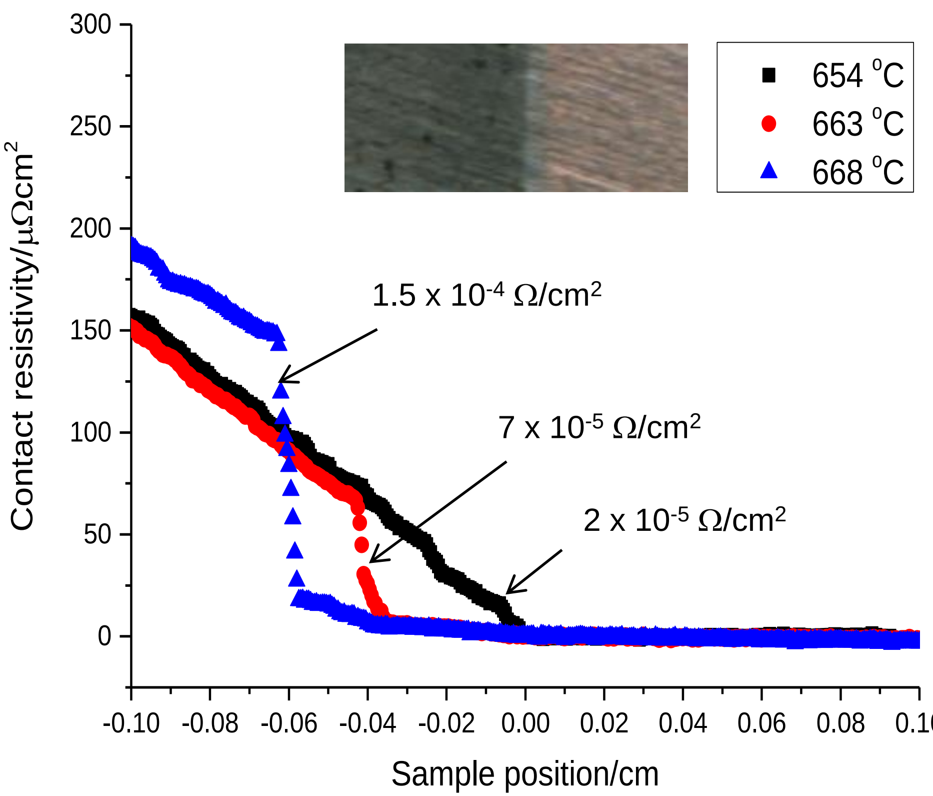
Spectrum	Co	Cu	Zn	Ag	Sb	Total
Spectrum 1	12.29	2.39	0.00	1.93	83.39	100.00
Spectrum 2	3.64	34.17	7.50	14.78	39.90	100.00
Spectrum 3	0.00	97.59	0.00	0.00	2.41	100.00

EDX analysis confirms the formation of the alloying region, which needs to be minimised in good TE modules.

Influence of Brazing Temperature on Interface Quality

INFLUENTIAL FACTORS

- Brazing temperature
- Brazing atmosphere
- Brazing materials
- Thermoelectric materials
- Barrier layers



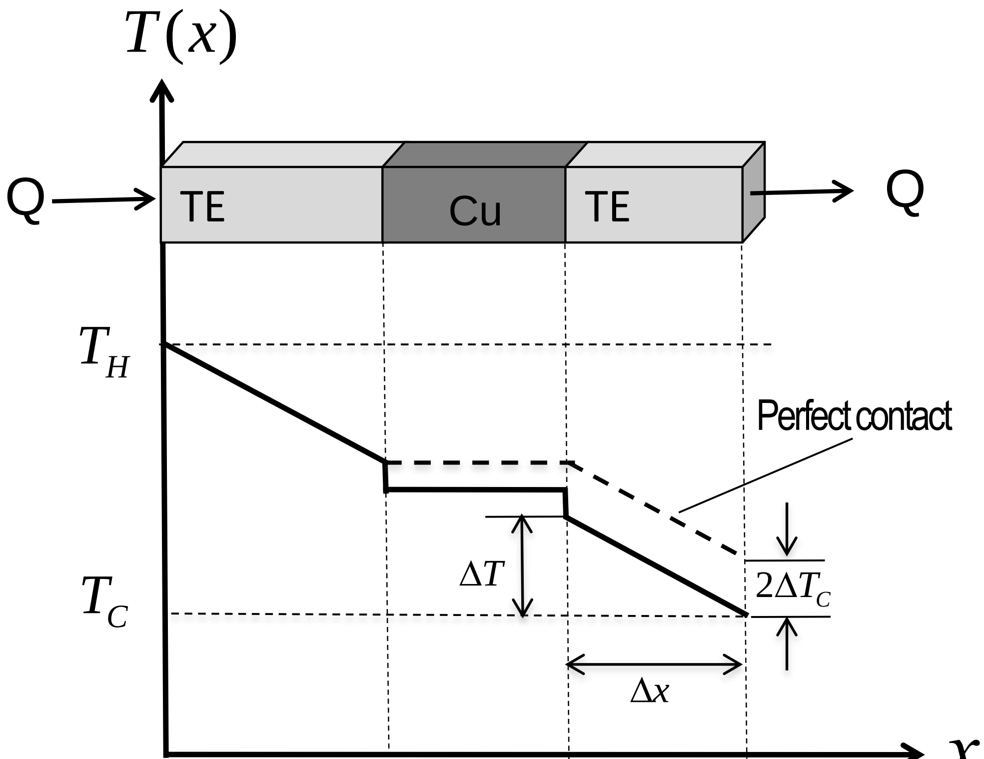
Thermal Contact – Principle of Measurement

Ensure constant heat flow through the sample:

$$\kappa \cdot A \frac{\Delta T}{\Delta x} = \kappa_c \cdot A \cdot \Delta T_c$$

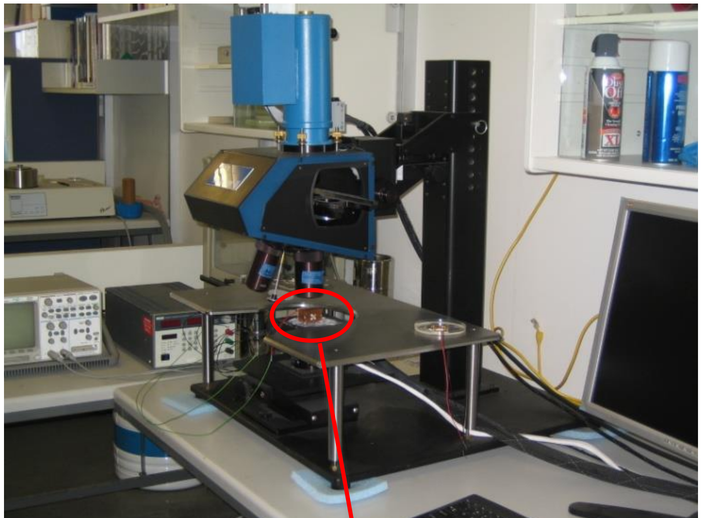
Given k of TE materials and determine ΔT, Δx, and ΔT_c:

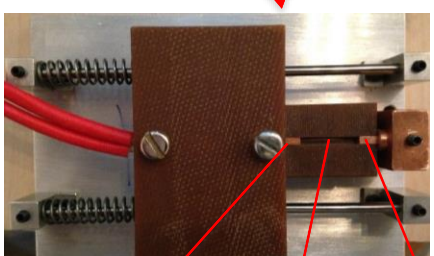
$$\kappa_c = \frac{k}{\Delta T_c} \cdot \frac{\Delta T}{\Delta x}$$



G Min and M Phillips, 2016, "Preparation and Characterisation of TE Interface" Chapter 6 in Thermoelectric Energy Conversion (Eds. Pineda & Rezania, Wiley-Vch), 111-125

Evaluation of Thermal Contact using IR Microscopy

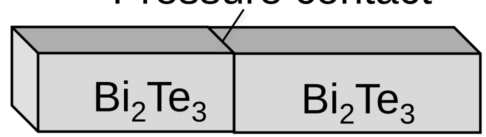


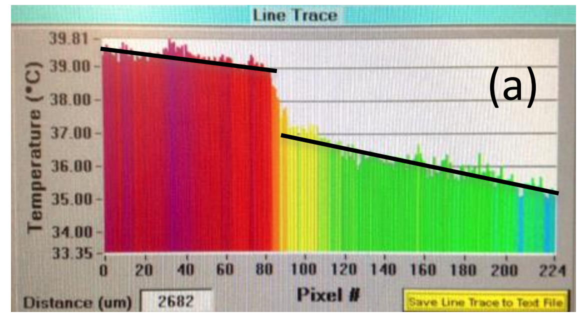


Hot contact

Sample

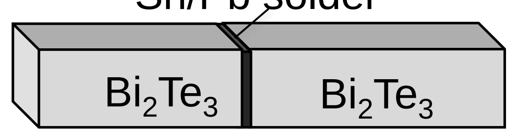
Cold contact

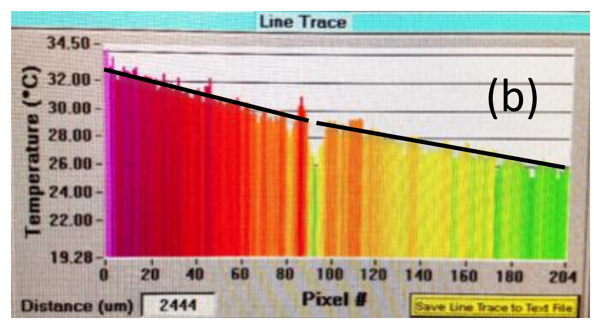




$$2.4 \times 10^3$$

$$(W/m^2K)$$





$$4.2 \times 10^4$$

$$(W/m^2K)$$

Similar results obtained using indium or heat sink compound

Thermoelectric Module Assembly Process

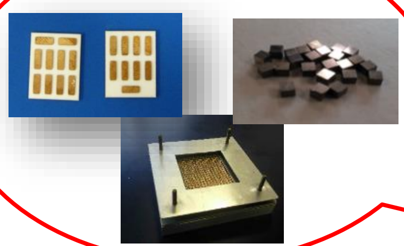
DESIGN

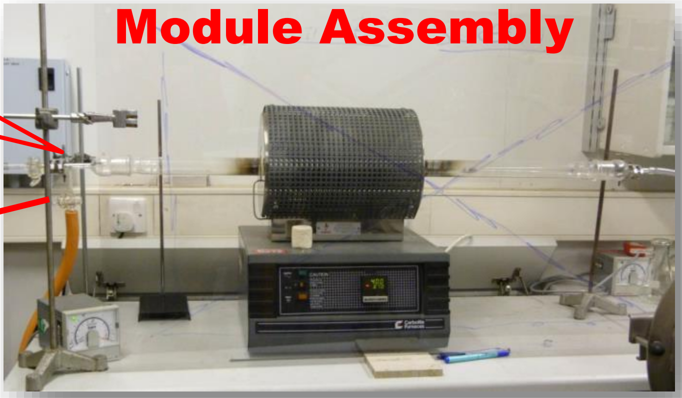
Ceramic substrate → Metallisation

Assembly rig
Bracing materials

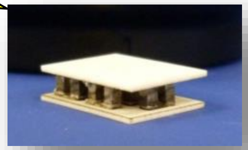
Cutting TE legs → Coating barrier layers

ASSEMBLY



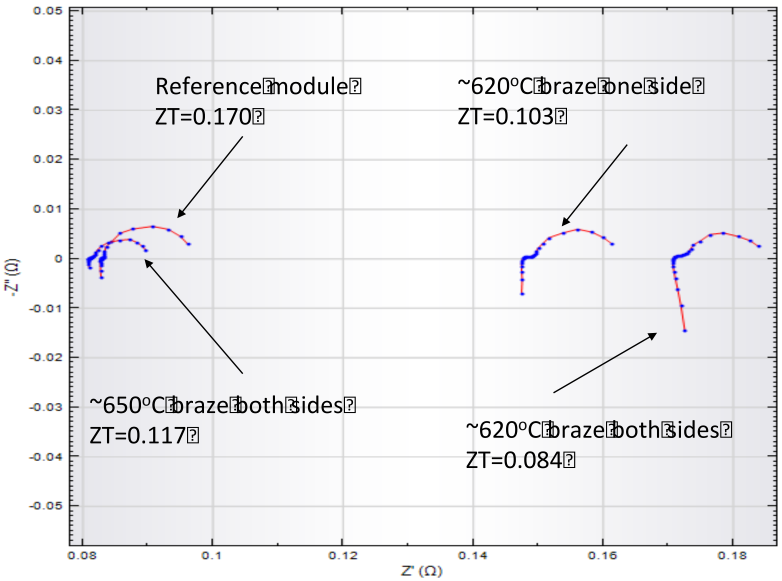


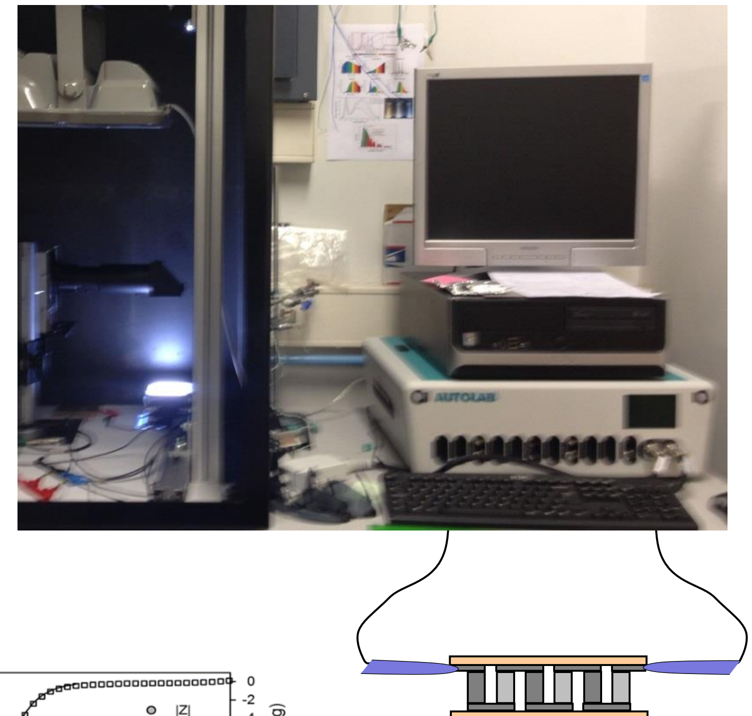
High Temperature
Skutterudite Module
by CU-RU-LU



J Garcia-Canadas, A Powell, A Kaltzoglou, P Voqueiro and G Min, Journal of Electronic Materials, (2013), 42(7), 1369-137

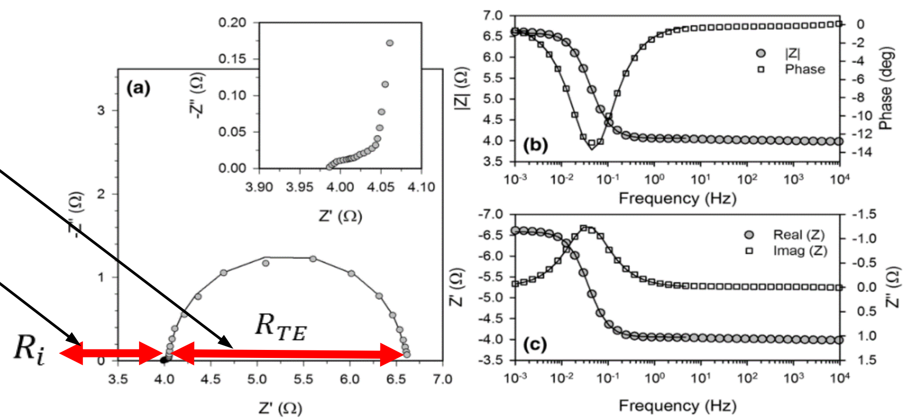
Rapid Screening by Thermoelectric Impedance Spectroscope





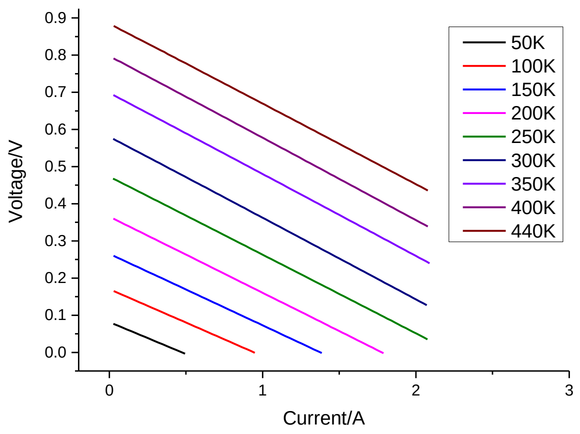
TE module

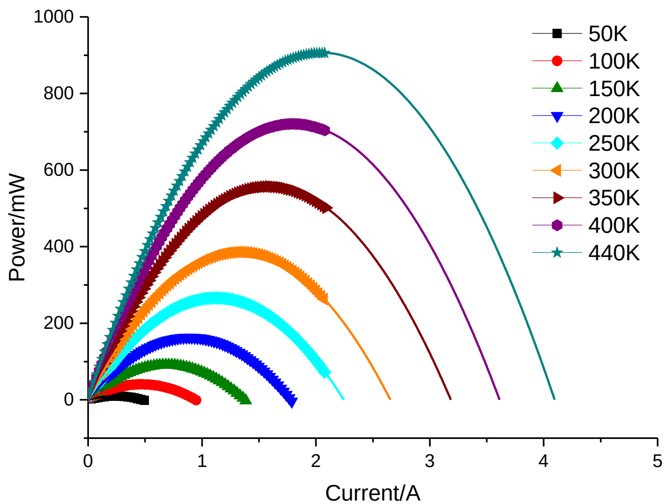
$$ZT = \frac{R_{TE}}{R_i}$$

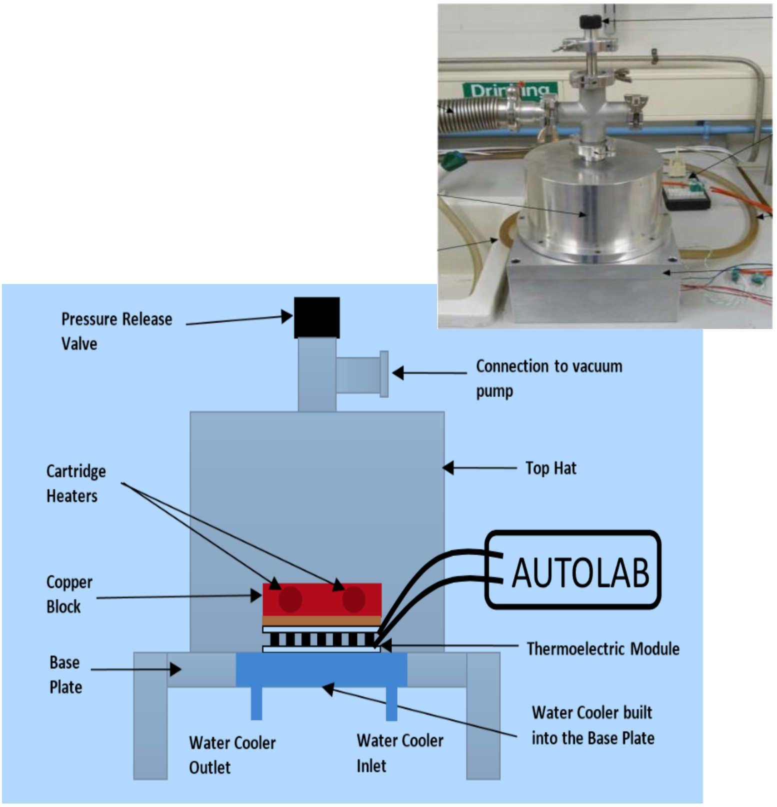


J. Garcia-Cañadas and G. Min, "Impedance Spectroscopy for Thermoelectric Characterisation" J. Appl. Phys. 116 (17), 174510 (2014).

Determination of Power Output by I-V Curves





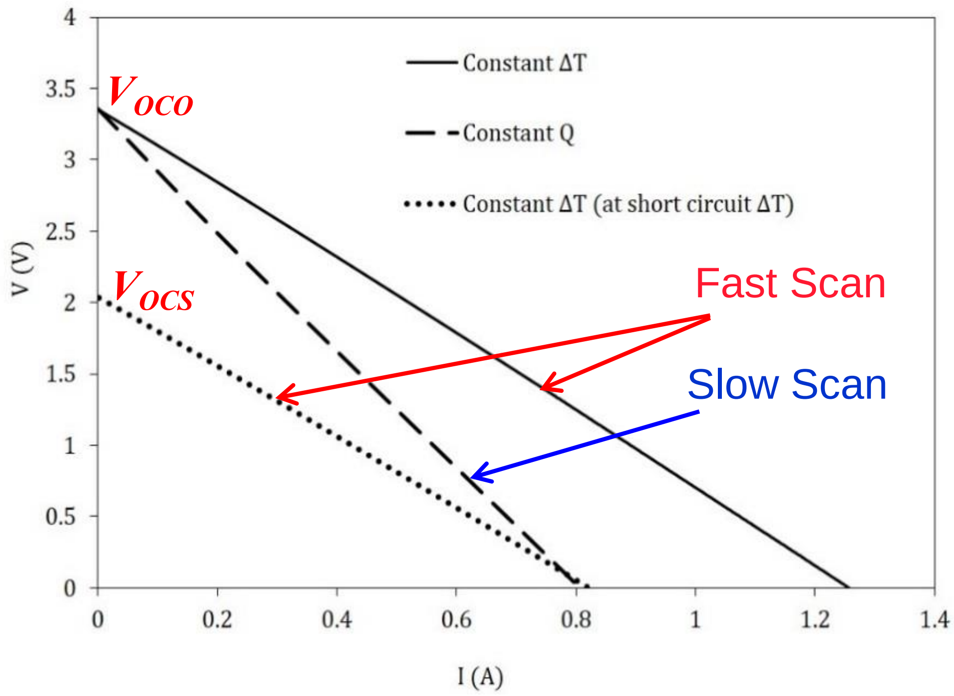


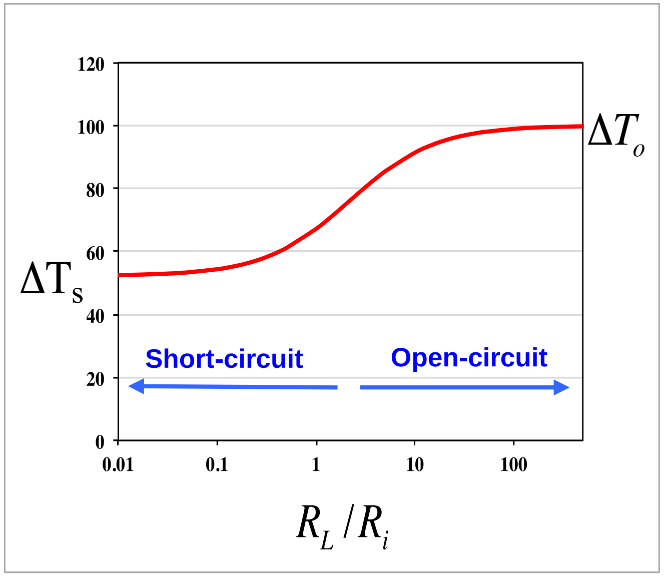
Be aware of errors when used for determining conversion efficiency

Determine Conversion Efficiency by Triple I-V Curves

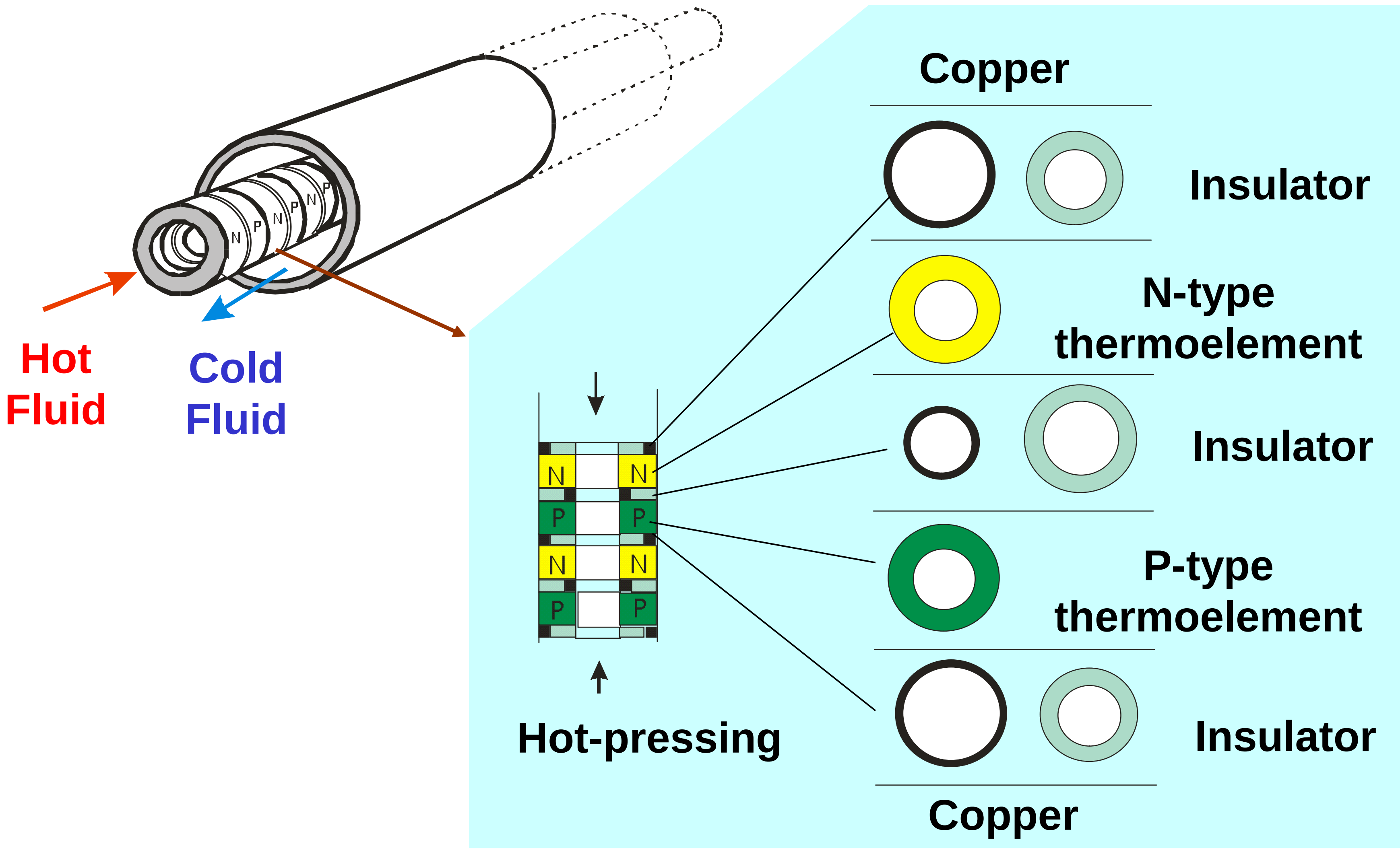
$$\eta_{max} = \frac{1}{4} \cdot \frac{\Delta T_o}{\bar{T}} \cdot \left(1 - \frac{V_{OCO}}{V_{OCS}}\right)$$

- V_{OCO} - corresponding to the first fast scan
- V_{OCS} - corresponding to the second fast scan
- *Fast Scan* – constant temperature difference
- *Slow Scan* – constant heat flux

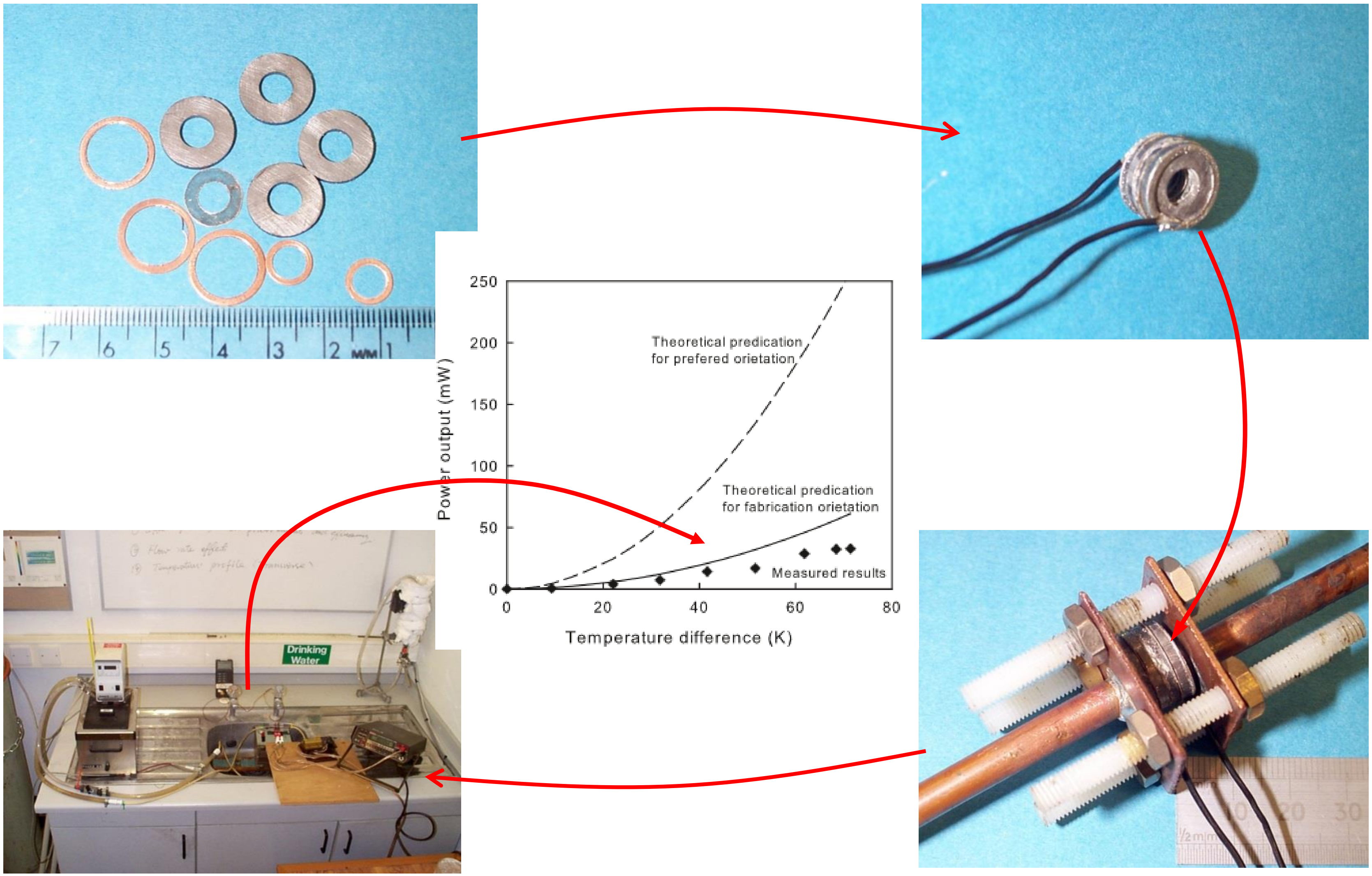




Ring-structured Thermoelectric Module



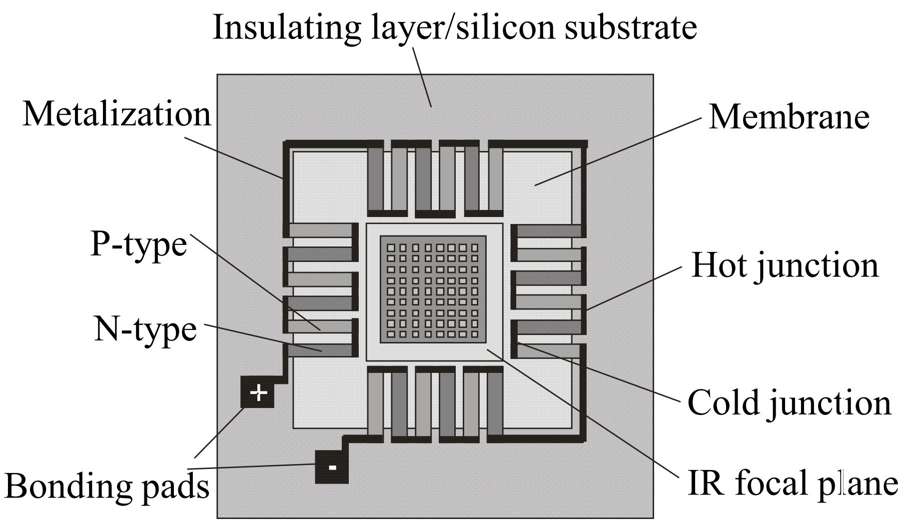
Ring-Structured Thermoelectric Tube

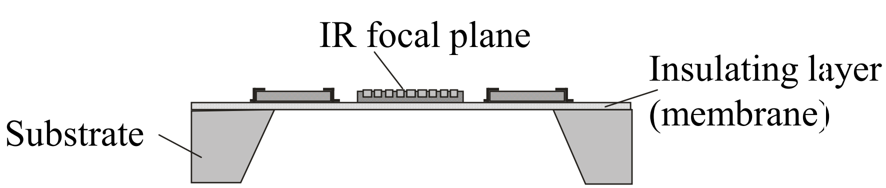


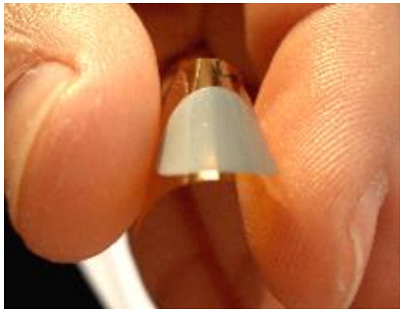
Gao Min and Rowe, 2007, Semicond. Sci. Technol., (27) 21-28

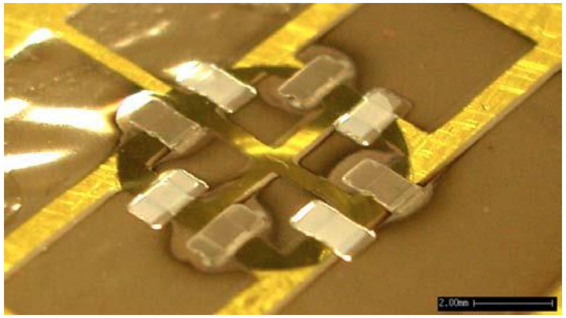
Micro/Nano Converters for Integrated Circuits

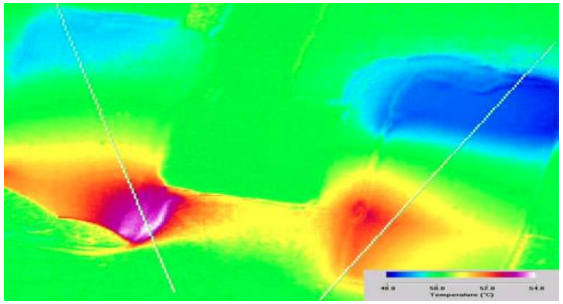
Horizontal structure











Ref: G Min and D Rowe, Electronics Letter, 1998, 34(2), 222-223

L.M. Goncalves. P. Alpuim, G. Min, D. M. Rowe, C. Couto, and J. H. Correia, "Optimization of Bi2Te3 and Sb2Te3 thin films deposited by co-evaporation on polyimide for thermoelectric applications", Vacuum, 82 (12), (2008), 1499-1502

Thank You

Acknowledgements

Dr. Matthew Philips, Dr. Jorge Garcia-Canadas and Dr. Tanuji Singh

The work is funded by the United Kingdom Engineering and Physical Science Research Council (EPSRC) under the projects of EP/K029142 and EP/K022156.