

# Mechanical properties of thermoelectric materials

Dr Hugo Williams

Ramy Mesalam

[hugo.williams@le.ac.uk](mailto:hugo.williams@le.ac.uk)



# Authors and acknowledgements

Hugo Williams, Ramy Mesalam, Richard Ambrosi and the Radioisotope Power Systems team  
*Department of Engineering and Department of Physics & Astronomy*  
*University of Leicester*

Mike Reece, Kan Chen, Huanpo Ning  
*Queen Mary University of London*



Kevin Simpson, Mark Robbins and team  
*European Thermodynamics Ltd., Kibworth, Leicestershire*



Keith Stephenson  
*European Space Agency, ESTEC, Noordwijk, The Netherlands*

Colleagues at National Nuclear Laboratory and Airbus Defence  
and Space

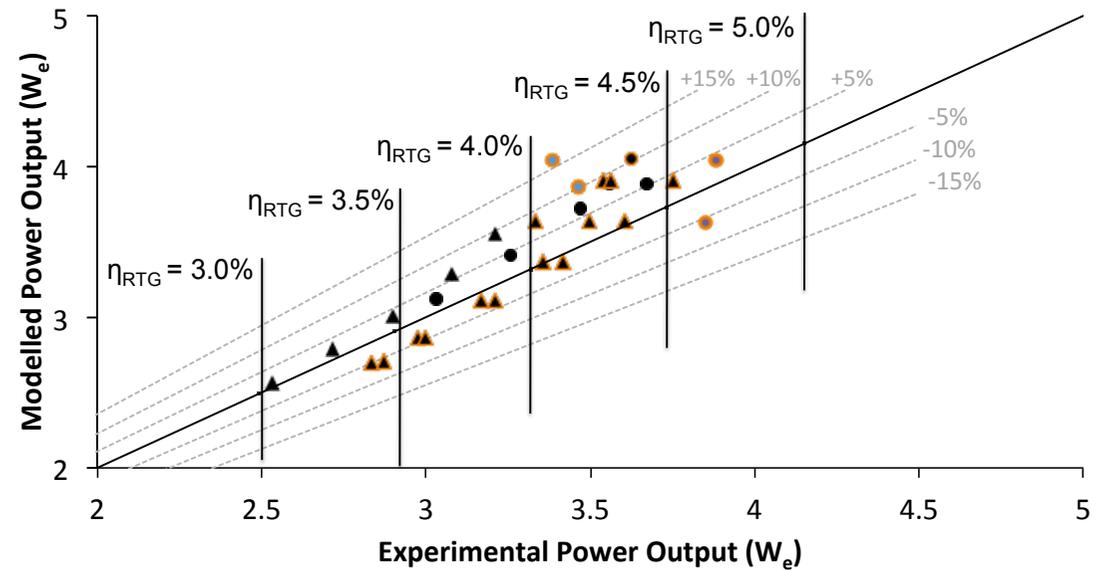
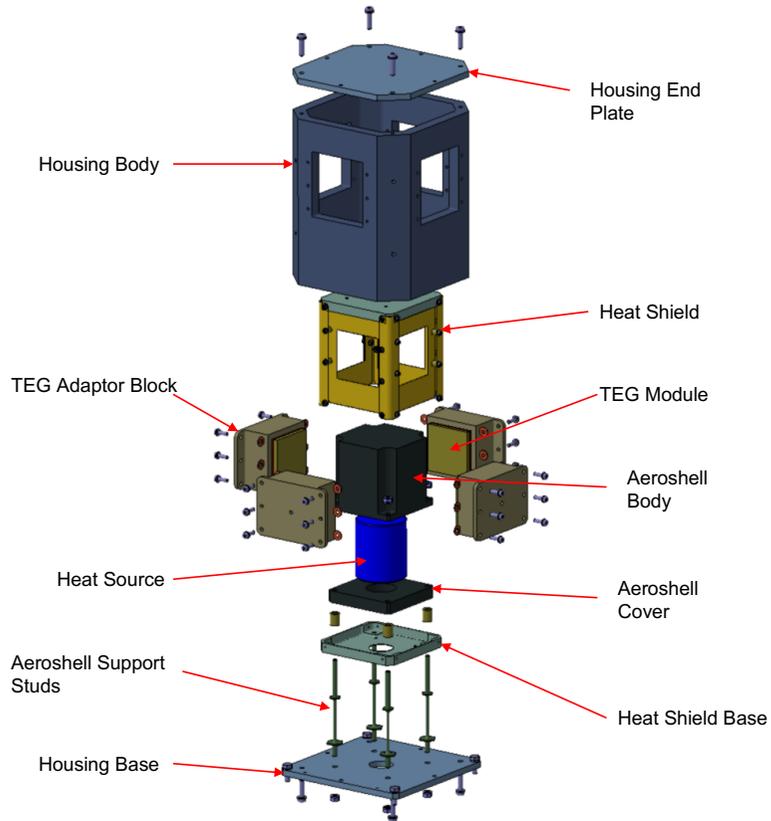
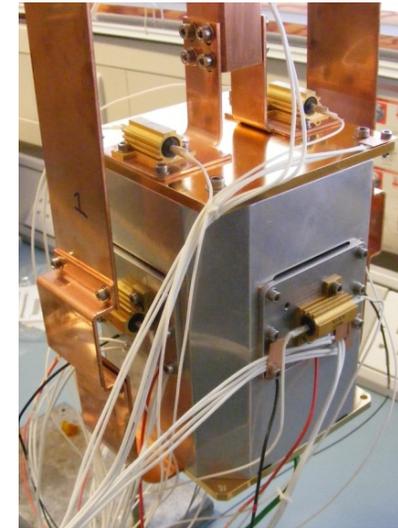
# Contents

- European Radioisotope Thermoelectric Generator (RTG) development
- Pilot study on mechanical property enhancement using SPS and nano-B<sub>4</sub>C.
- Mechanical challenges for Space RTGs
- Research challenges and future perspective

# RTG Development in the UK

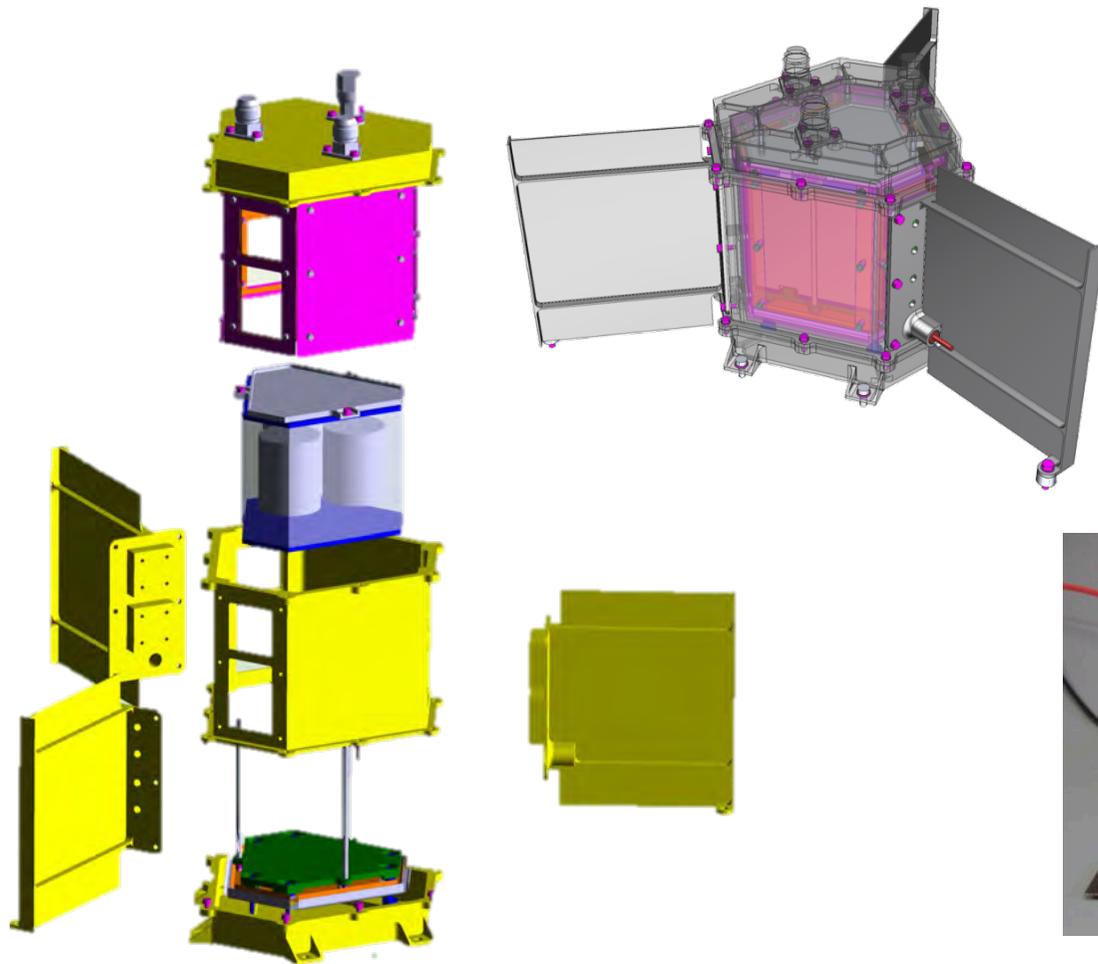
- UoL has led RTG development in UK under contract to ESA since 2010:
  - PI: Prof. Richard Ambrosi, UoL
- Aim: Develop a first iteration RTG design for Europe optimised for  $^{241}\text{Am}$  fuel
- Designed, built and tested a small-scale lab prototype:
  - Target power  $5 W_e$  from  $83 W_{th}$  (electrically heated)
  - Develop a test bed for the integrated system performance of thermoelectric materials & modules
- Produced a  $10 W_e$  refined flight design based on this architecture
- Next phase of work will be a 'breadboard' for the refined flight design

# RTG Laboratory prototype



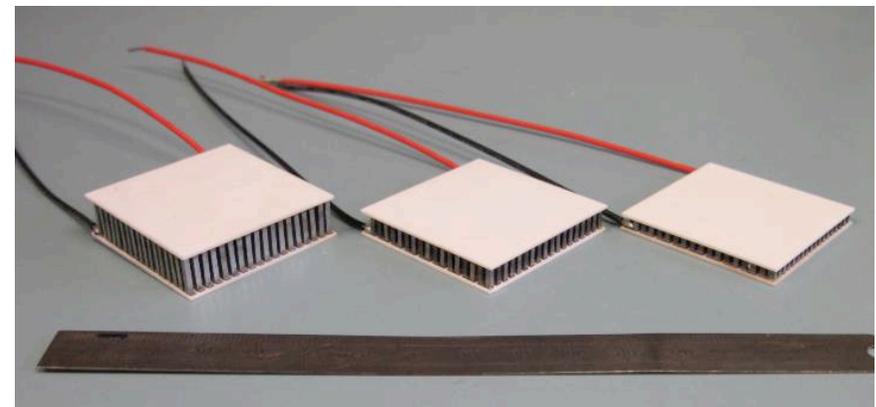
- 6 mm, Ti heatshield
- ▲ 8 mm, Ti heatshield
- 6 mm + Au heat shield
- ▲ 8 mm, Au heatshield
- 6 mm BST, Au heat shield
- 6 mm BST + B4C, Au heat shield

# RTG Architecture & implications



For the thermoelectrics:

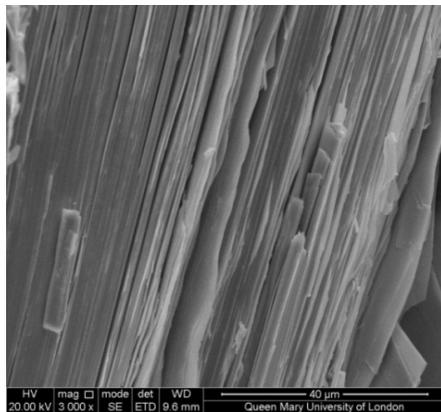
- $\text{Bi}_2\text{Te}_3$  based materials
- Compression & shear loading
- Modules with high aspect ratio legs



# Enhanced $\text{Bi}_2\text{Te}_3$ thermoelectrics

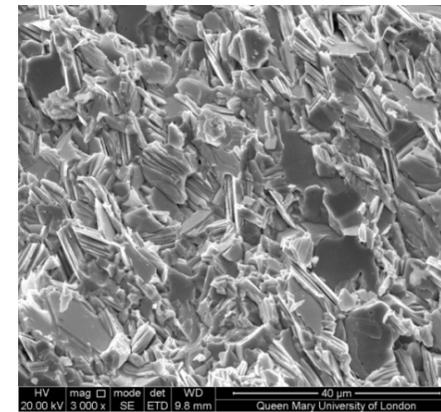
- Most active research on thermoelectric materials focuses on zT
- Mechanical properties and behaviour of materials and modules is under-represented in the literature.

Conventional material production is by directional solidification



Very poor strength and/or toughness  
← due to cleavage along the basal crystallographic plane // to growth

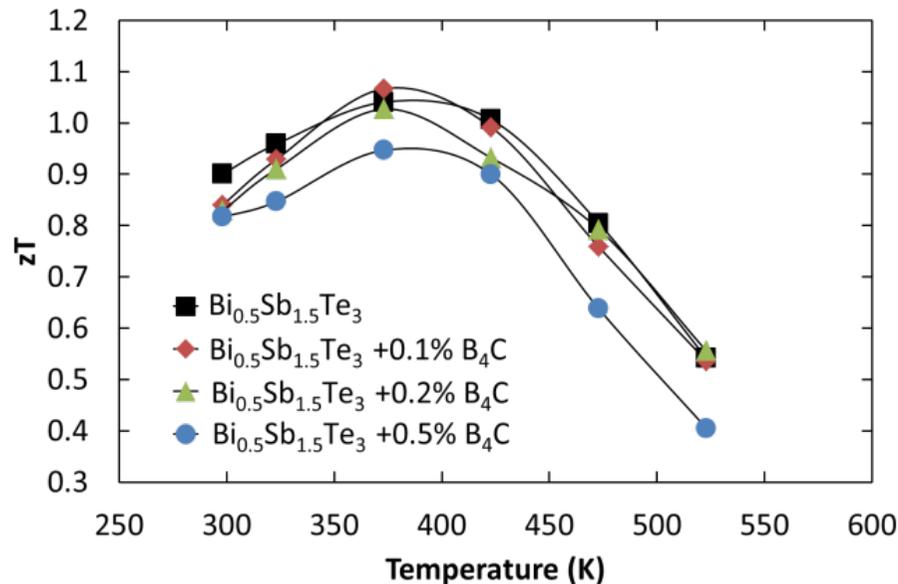
Polycrystalline, fine grained materials: better mechanical properties



Williams HR et al. 2015. Spark Plasma Sintered bismuth telluride-based thermoelectric materials incorporating dispersed boron carbide. *Journal of Alloys and Compounds*. **626**. 368-374.

# Enhanced $\text{Bi}_2\text{Te}_3$ thermoelectrics

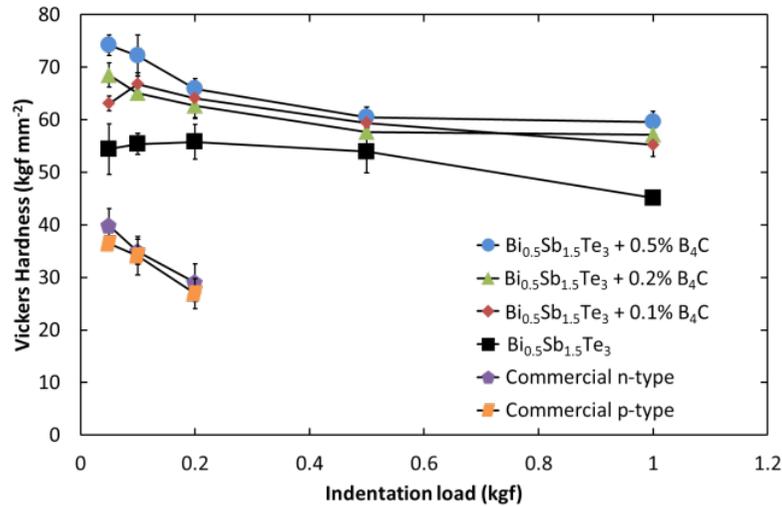
- Literature indicates that addition of small volume fraction of nanoscale particles can enhance mechanical properties further and maintain/increase  $zT$ .
- Nano-scale  $\text{B}_4\text{C}$  added at up to 0.5 vol% to p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  produced by mechanical alloying and Spark Plasma Sintering (SPS).



- p-type selected because generally more mechanically challenging than n-type
- Up to 0.2 vol%  $\text{B}_4\text{C}$  the effect on  $zT$  is negligible.

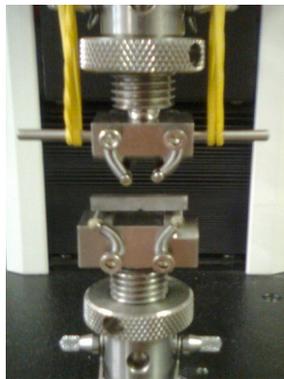
Williams HR et al. 2015. *Journal of Alloys and Compounds*. **626**. 368-374.

# Enhanced $\text{Bi}_2\text{Te}_3$ thermoelectrics

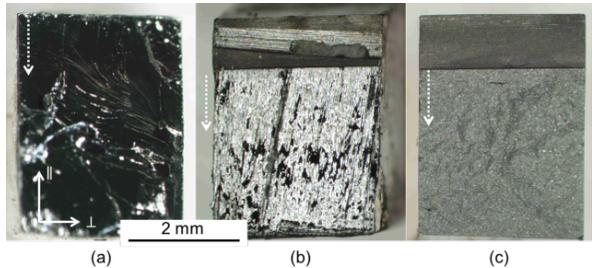


- Addition of nano-scale  $\text{B}_4\text{C}$  significantly improved Vickers hardness over and above the benefit of a polycrystalline material.
- Fracture toughness also measured for polycrystalline material, conventional materials were so brittle that few valid failures were obtained

First SEVNB measurement of  $\text{Bi}_2\text{Te}_3$  materials:



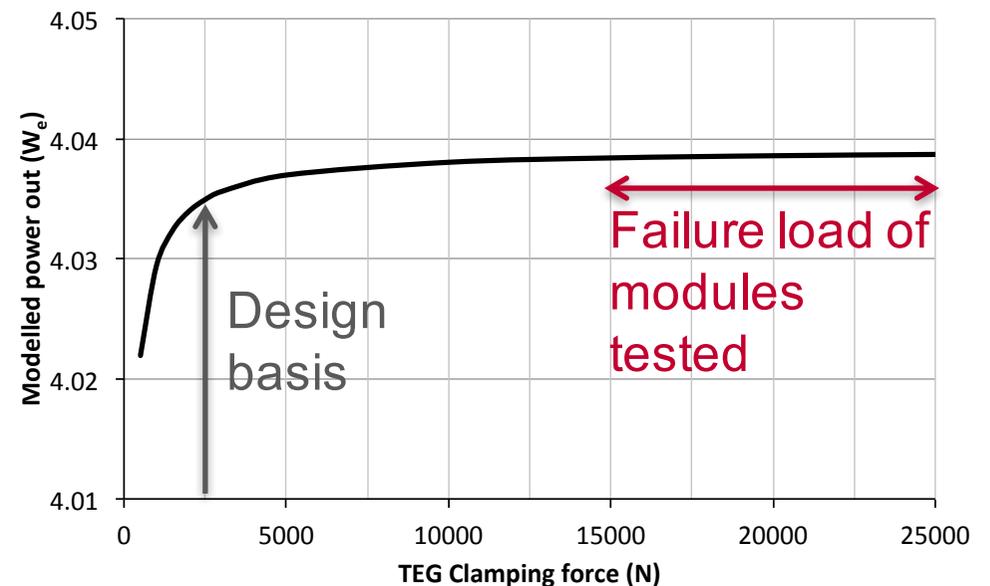
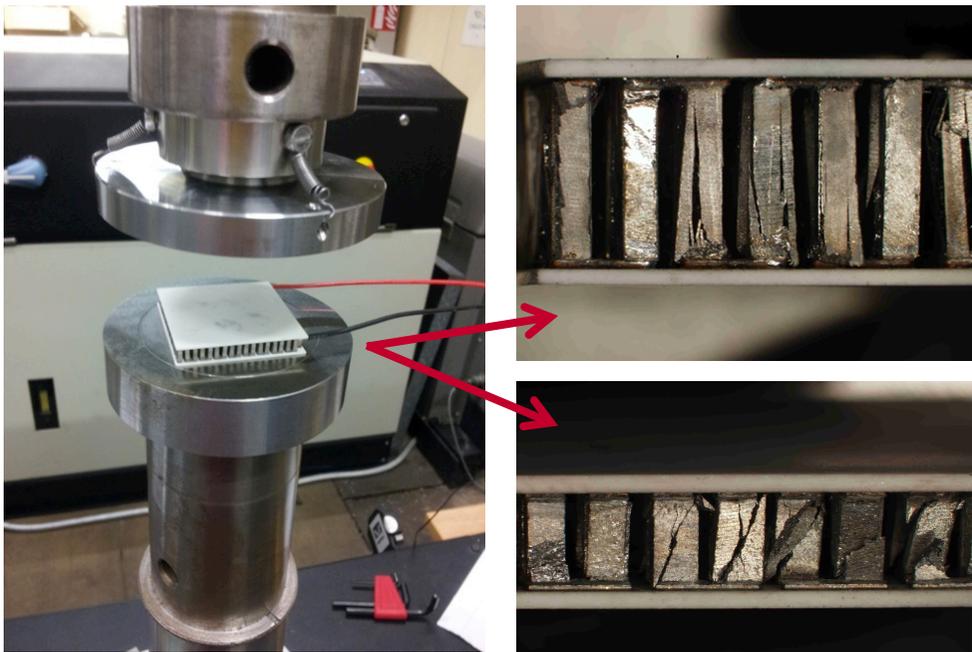
Material	Fracture toughness $K_{Ic}$ ( $\text{MPa m}^{1/2}$ ) $\pm 1\sigma$
Conventional Directional Solidified	Invalid failures
SPS	$0.79 \pm 0.03$
SPS + 0.2 vol% $\text{B}_4\text{C}$	$0.80 \pm 0.01$



Williams HR et al. 2015. *Journal of Alloys and Compounds*. **626**. 368-374.

# Bi<sub>2</sub>Te<sub>3</sub> module mechanical integration

- Manufacture challenges for long legs with conventional materials
- RTG efficiency is linked to static compression strength of modules:
  - Study suggests good thermal conduction well within compression capability of modules, even with conventional materials
- Launch vibration imposes compression and shear



# Mechanical Properties of Interest

## Machinability

Reduce Strength Limiting Flaws!

$$\propto \left( \frac{HE}{(K_{IC})^2} \right)^{-1}$$

Reduce Brittleness Index

## Thermomechanical Response

Thermoelastic Approach

$$R = \frac{\sigma_f k (1 - \nu)}{E \alpha_{CTE}}$$

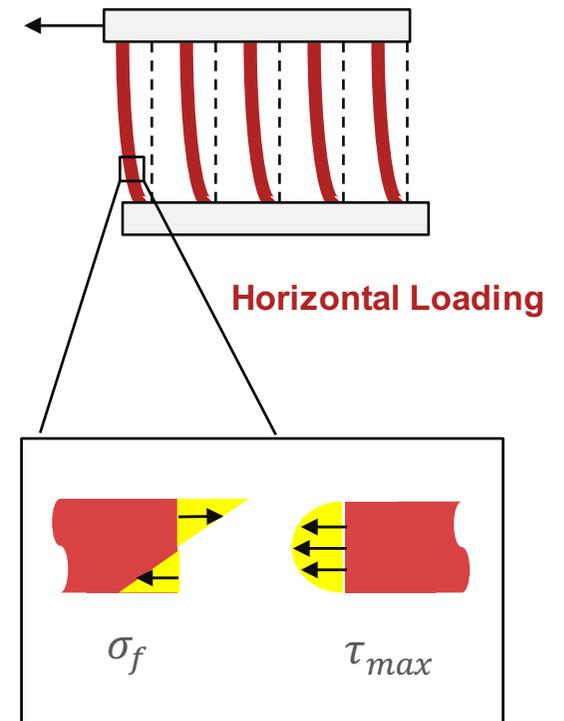
Energy Balance Approach

$$R = \frac{K_{IC} (1 - \nu^2)^{0.5}}{E \alpha_{CTE}}$$

Increase Resistance Index

## Modal Response

$$([K] - \omega^2 [M])\{\varphi\} = 0$$



# Mechanical Characterisation of Thermoelectric Materials

	Property	Procedure	Coupon Size	Sample Size	Statistical Analysis
$\sigma_f$	Flexural Strength	ASTM C1161 (4pt-Bending)	1.5 x 2.0 x 25 mm <sup>3</sup>	30	Weibull
$K_{Ic}$	Fracture Toughness	ISO 23146 (SEVNB)	3.0 x 4.0 x 25 mm <sup>3</sup>	30	Weibull
E	Elastic Modulus	ISO 14577 (Nanoindentation)	N/S	30	Gaussian
H	Hardness	ASTM C1327 (Vickers Ind)	N/S	30	Gaussian

Supporting crystallography (e.g. XRD) and Fractography (SEM)

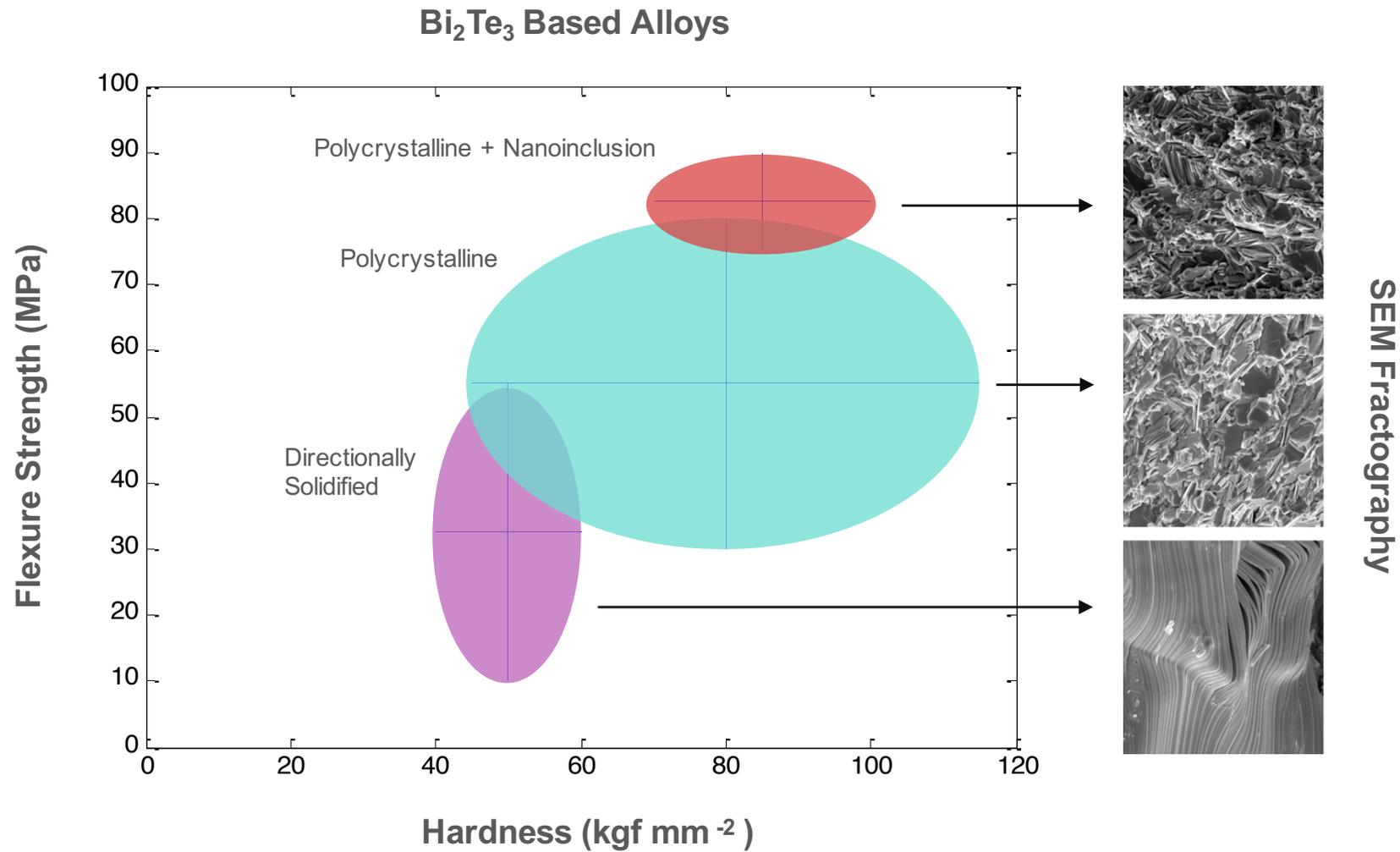
Sample size for full 'flight' qualification – research studies in literature have used using smaller specimen groups

# Polycrystalline & enhancements

Research group	Year	Thermoelectric Material	Processing Method	Enhancement Mechanism	Fracture Toughness improvement (%)	ZT Improvement (%)
Duan et al.	2012	$\text{CoSb}_{2.875}\text{Te}_{0.125}$	BM-SPS	$\text{nano}_p\text{-TiN}$	40	10
Schmidt et al.	2015	$\text{Mg}_2\text{Si}$	BM-SPS	$\text{nano}_p\text{-SiC}$	33 <sup>v</sup>	NS
Zhao et al.	2008	$\text{Bi}_2\text{Te}_3$	MA-BM-SPS	$\text{nano}_p\text{-SiC}$	18 <sup>v</sup>	2
Liu et al.	2010	$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	BM-SPS	$\text{nano}_p\text{-SiC}$	12 <sup>v</sup>	10*
Duan et al.	2014	$\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$	BM-SPS	$\text{nano}_p\text{-Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$	11	0
Akao et al.	2014	$\text{Zn}_4\text{Sb}_3$	BM-HP	$\text{nano}_w\text{-SiC}$	10 <sup>v</sup>	-30
Akao et al.	2014	$\text{Zn}_4\text{Sb}_3$	BM-HE	$\text{nano}_w\text{-SiC}$	9 <sup>v</sup>	-30
Wan et al.	2015	$\text{CeFe}_4\text{Sb}_{12}$	MA-M-SPS	Short $C_f$	4	2

<sup>v</sup> Measured by Vickers indentation method

# The Current Trend



# Challenges and next steps

- Most thermoelectric development work reported is focused on  $zT$  enhancement.
- Literature on mechanical property enhancement requires review and consolidation, but there are promising approaches for improving properties
- Critical mechanical properties are almost certainly different for different configurations of thermoelectric device.
- Larger test campaigns will be required to generate statistically meaningful data for engineering application.
- In published literature, the direction of mechanical (and thermoelectric) property measurements is often not clearly stated, making comparisons difficult!
- **Next phase of ESA project at UoL (working with QMUL/ETL) will investigate n-type  $\text{Bi}_2\text{Te}_3$ -based material, but also develop wider mechanical testing expertise and capability which we hope will support wider thermoelectric applications.**

# Support slides: material orientations

