

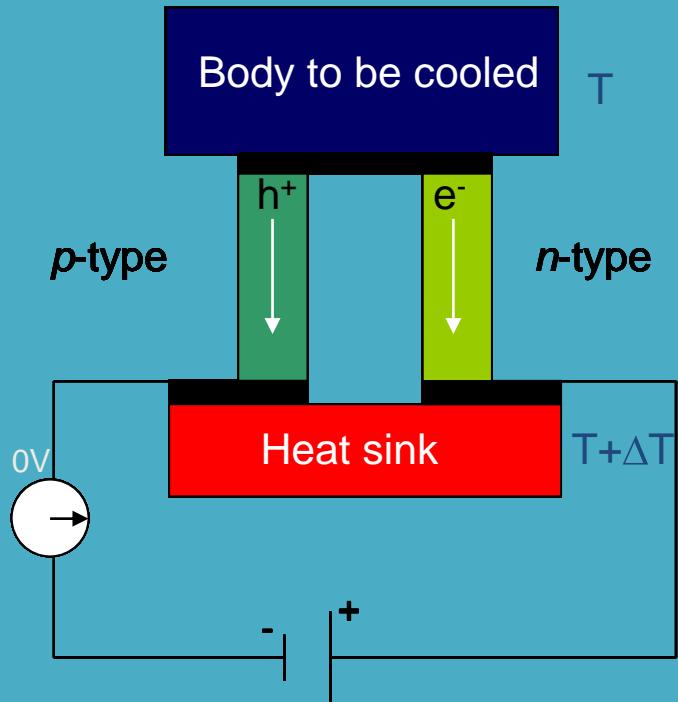
# Designing Next-Generation Thermoelectric Materials for Energy Harvesting

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# Thermoelectric Energy Recovery

Thermoelectric Couple

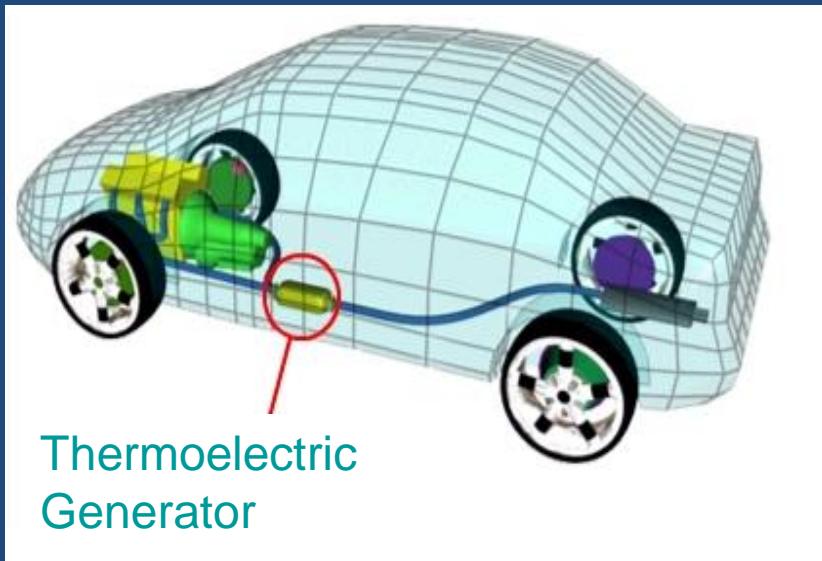


Power Generation



- Lightweight and small
- Very reliable

# Energy from Waste Heat



New car emission standards

160 g CO<sub>2</sub>/km (2007)

130 g CO<sub>2</sub>/km (2012)

95 g CO<sub>2</sub>/km (2020)

*Regulation (EC) No 443/2009 (2009)*

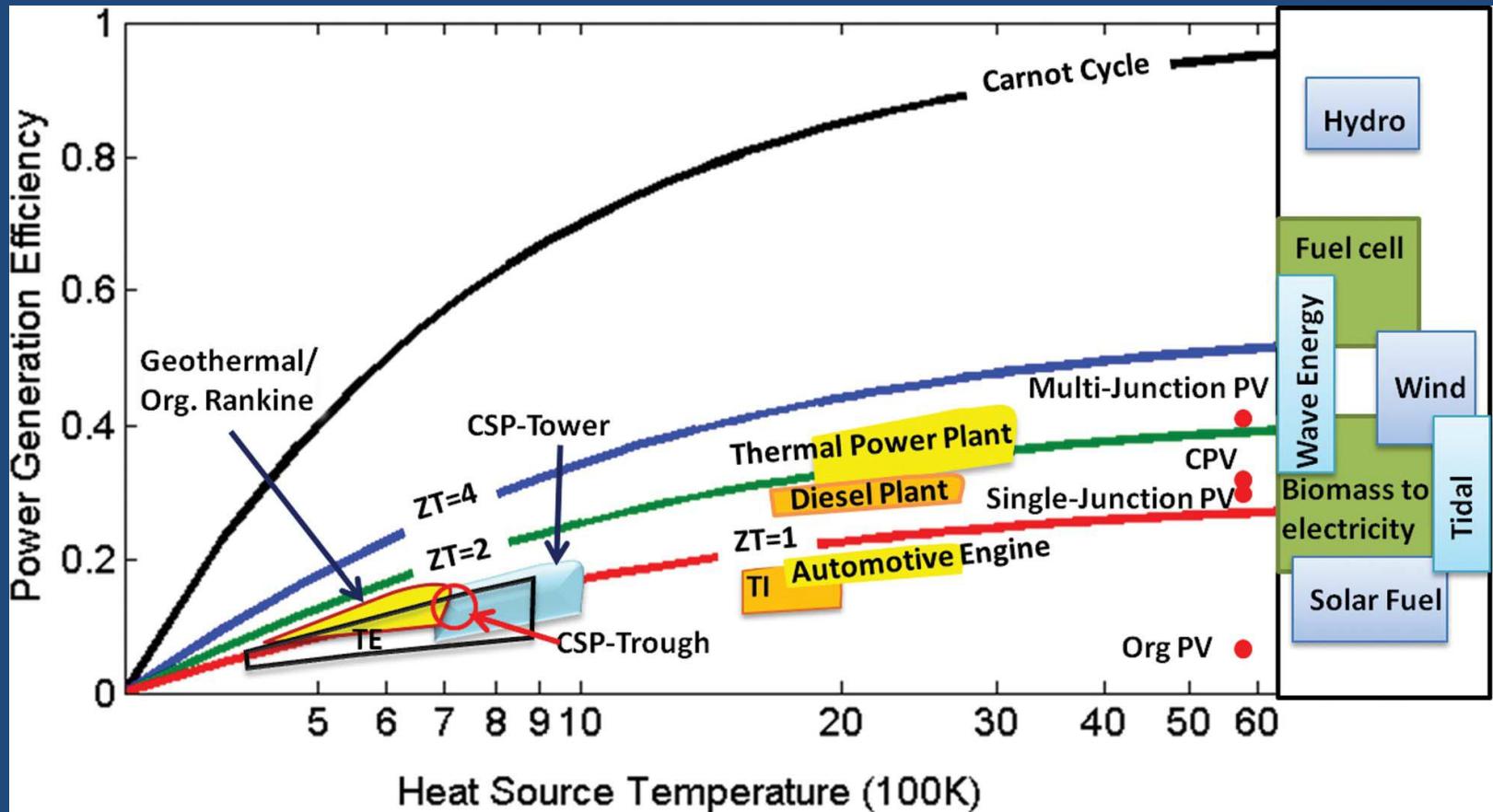
80% reduction in greenhouse gas emissions (from 1990 levels) by 2050  
*UK Climate Change Act (2008)*

Recent programs:  
GM  
BMW  
VW

} 200 - 600W TEG  
ca. 5% Fuel Economy



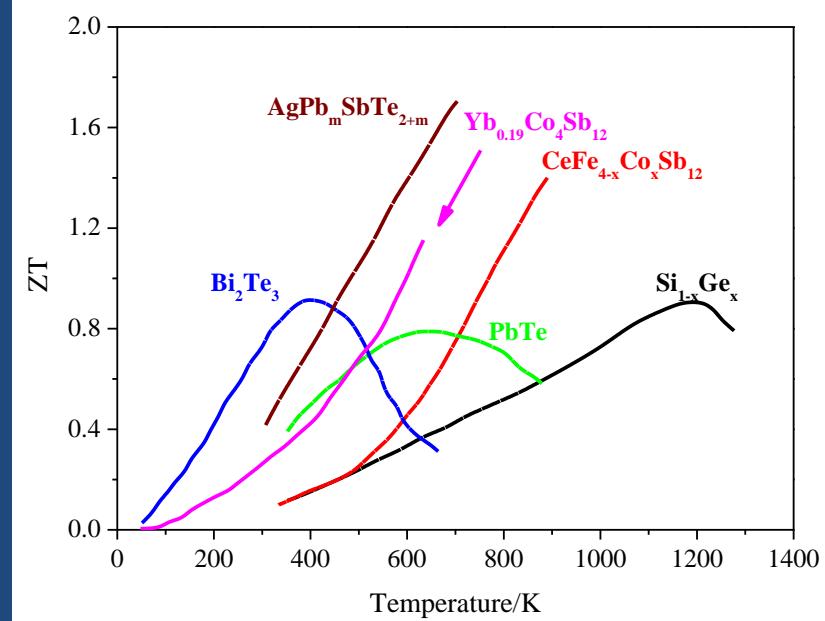
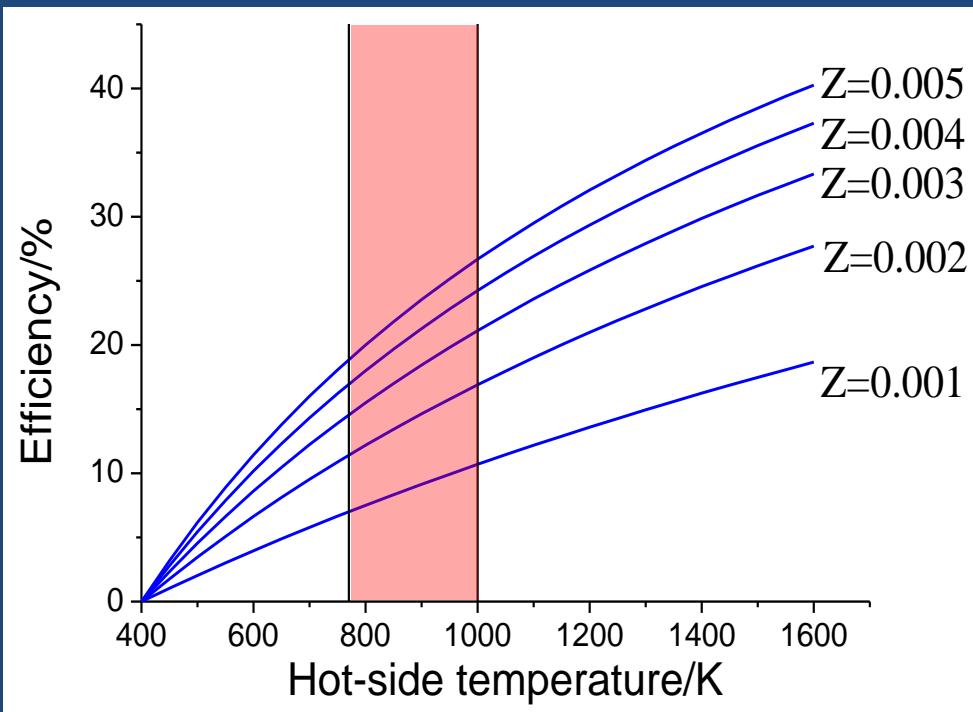
# Energy Conversion Technologies



# Limitations of Current Materials

Figure of Merit:

$$ZT = \frac{S^2 \sigma T}{(\kappa_L + \kappa_e)}$$

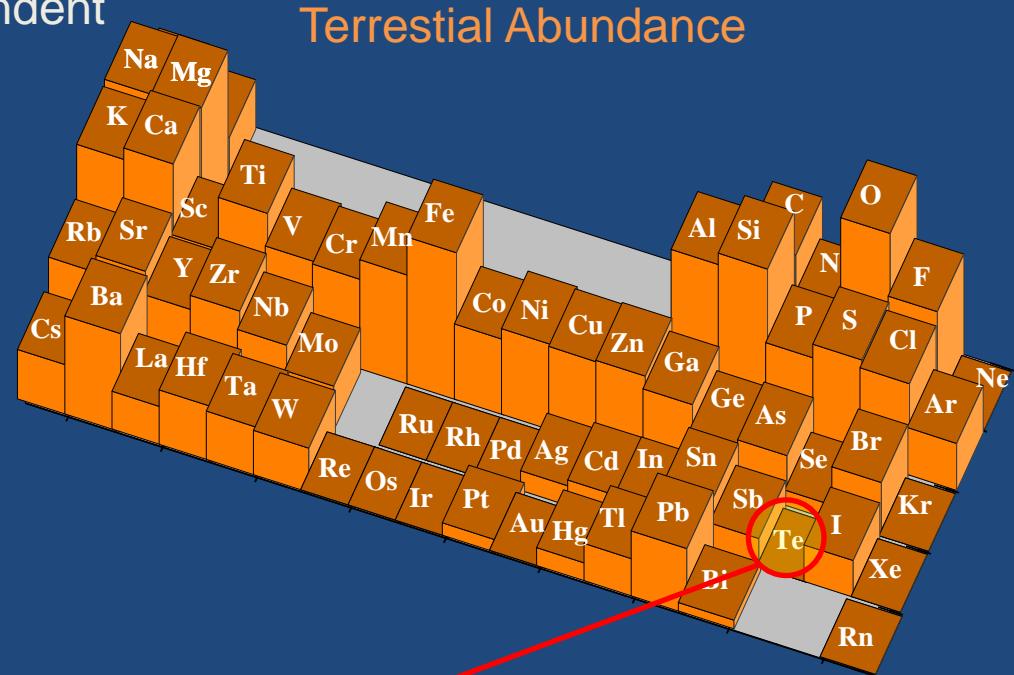
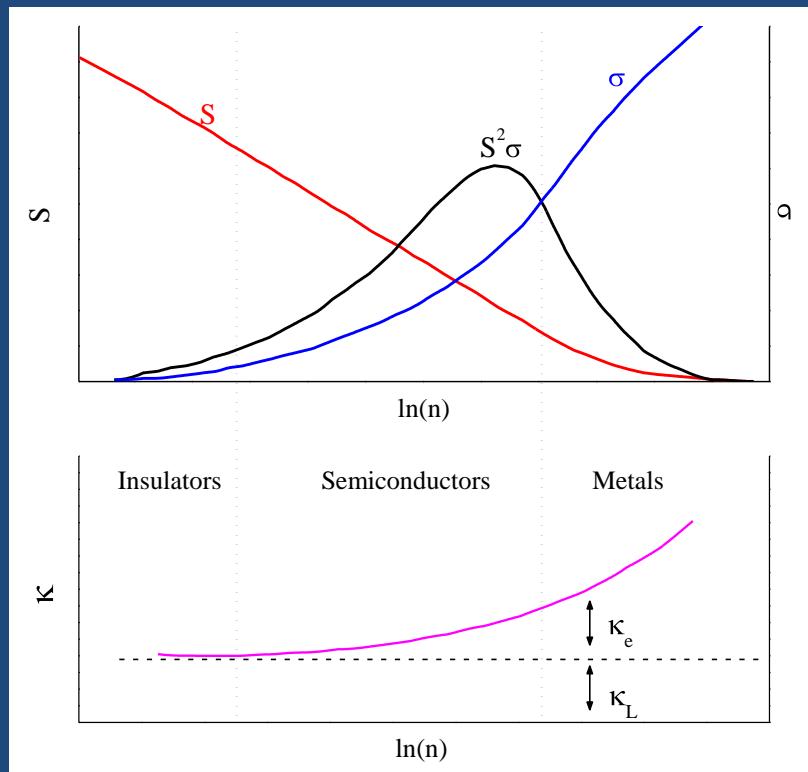


# Materials Parameters

Figure of Merit:

$$ZT = \frac{S^2 \sigma T}{(\kappa_L + \kappa_e)}$$

- Electrical conductivity ( $\sigma$ ), Seebeck (S) and electronic thermal conductivity ( $\kappa_e$ ) all inter-dependent

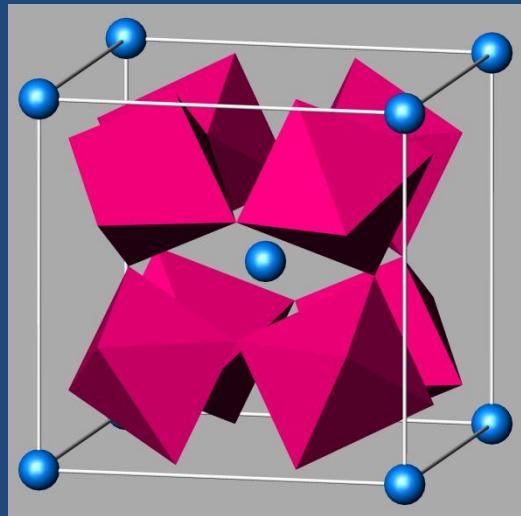


Te: 1 ppb by weight

Requires conduction of electricity like a metal and conduction of heat like an insulator

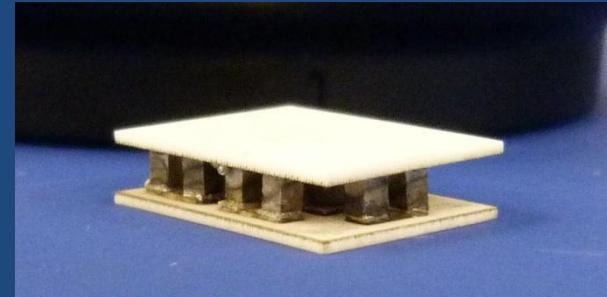
# Materials Design: Phonon Glass Electron Crystal

Filled Skutterudites



HWU-Cardiff Skutterudite Module

$\text{Yb}_x\text{Co}_4\text{Sb}_{12}$  (*n*-type)  
 $\text{Ce}_x\text{Fe}_3\text{CoSb}_{12}$  (*p*-type)



Rattling vibrations reduce  $\kappa_{\text{ph}}$

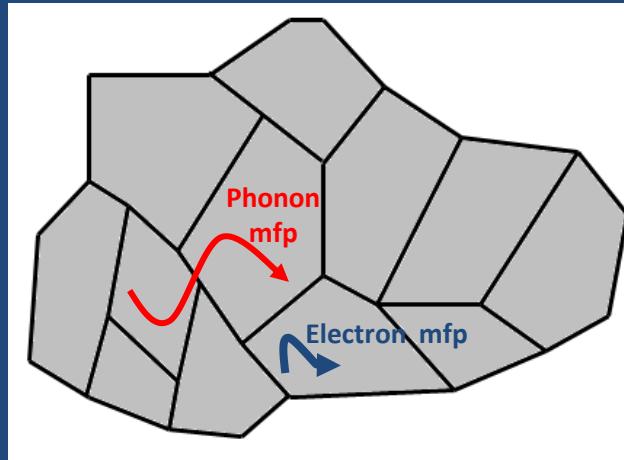
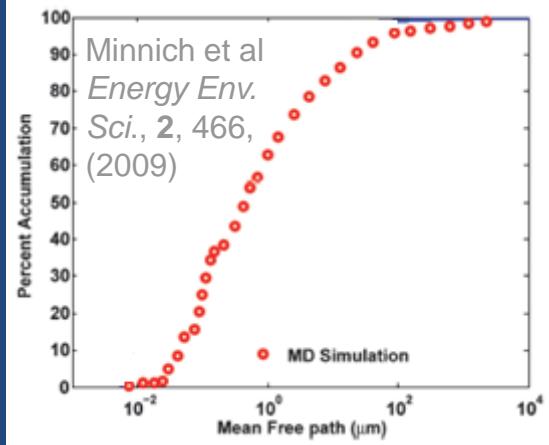
$\text{CoSb}_3$ :  $9 \text{ W m}^{-1}\text{K}^{-1}$

$\text{R}(\text{Fe}_3\text{CoSb}_{12})$ :  $1.2 \text{ W m}^{-1}\text{K}^{-1}$

- $3 \text{ W cm}^{-3}$  at  $\Delta T \approx 300 \text{ K}$  ( $T_{\text{cold}} = 293 \text{ K}$ )
- Compares favourably with  $\text{Bi}_2\text{Te}_3$   
 $(3 \text{ W cm}^{-3} \text{ at } \Delta T \approx 100 \text{ K} \text{ (} T_{\text{cold}} = 293 \text{ K) })$

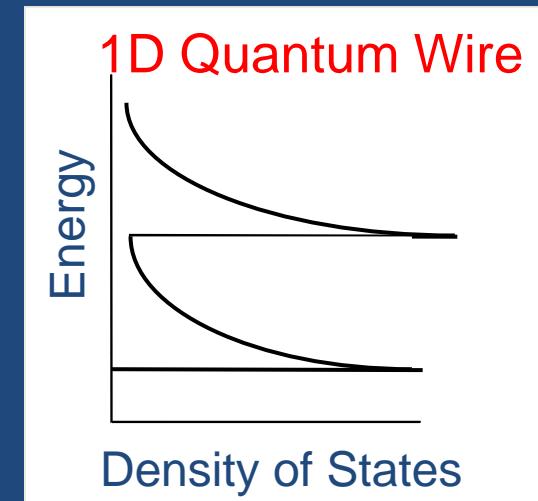
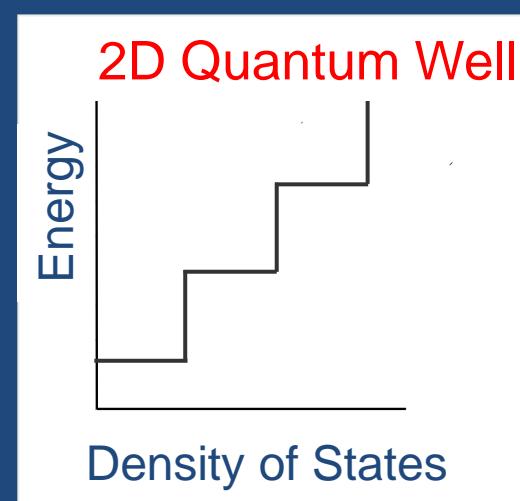
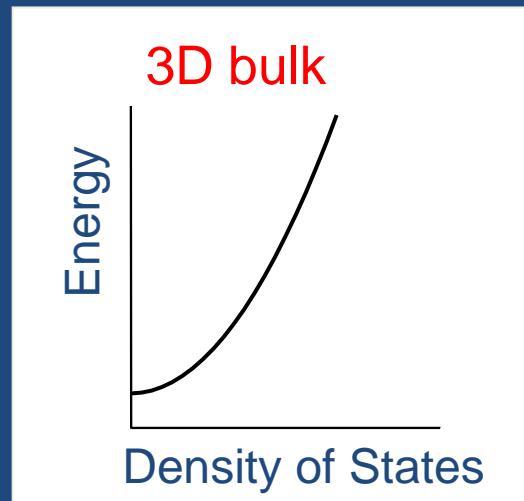
# Nanostructured Thermoelectrics

Interface Scattering: Decreases  $\kappa_L$

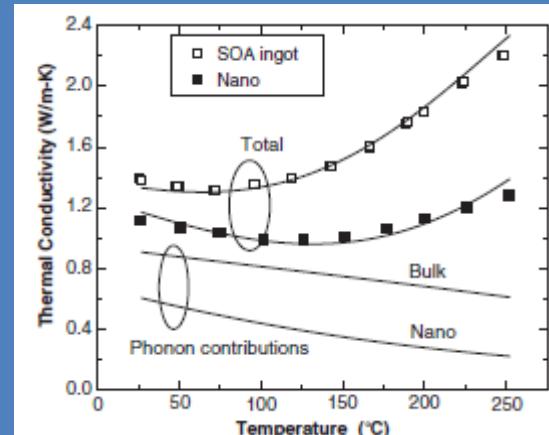
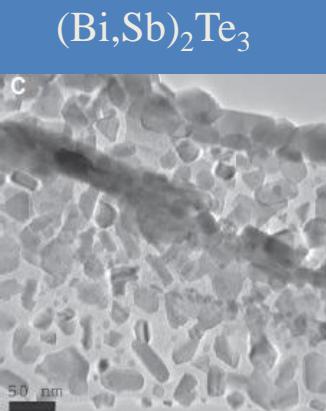
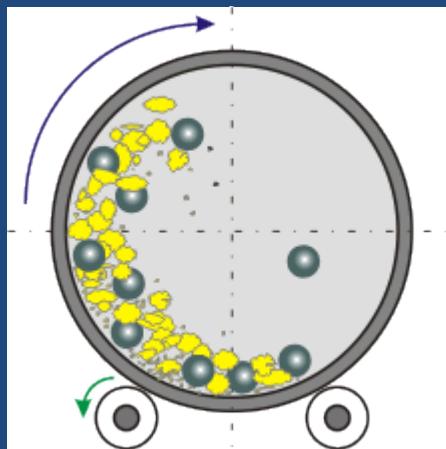


- Interface scattering when mean-free-path > interface spacing

Quantum Confinement: Enhances S



# Ball-Milled Thermoelectrics



Poudel et al, *Science*, **320**, 634, (2008)

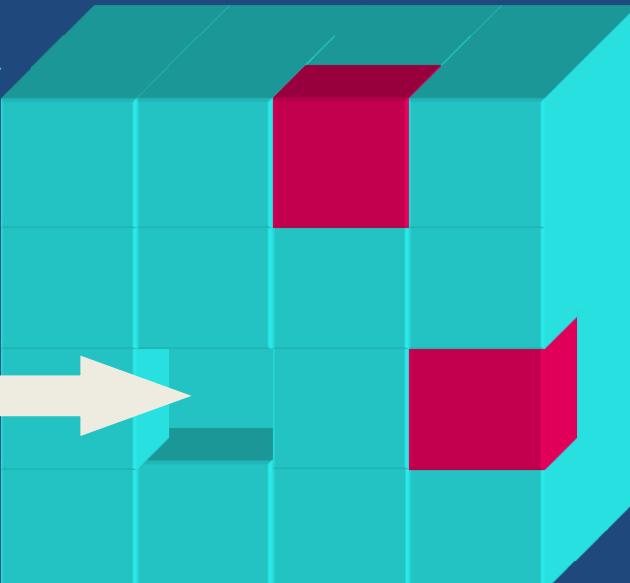
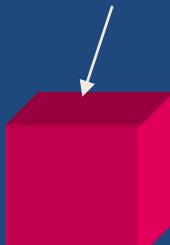
Material	Bulk		Nanostructured	
	$ZT_{\max}$	Temperature at which $ZT_{\max}$ is observed	$ZT_{\max}$	Temperature at which $ZT_{\max}$ is observed
Si	0.2	1200	0.7	1200
$\text{Si}_{80}\text{Ge}_{20}$ (n-type)	1.0	1200	1.3	1173
$\text{Si}_{80}\text{Ge}_{20}$ (p-type)	0.7	1200	0.95	1073
$(\text{Bi},\text{Sb})_2\text{Te}_3$	0.9	293	1.4	373
$\text{CoSb}_3$	0.45	700	0.71	700

# Nanoinclusions in *LAST*-type Phases



Pb rich matrix

A/B rich  
Nanocluster



- Degenerate semiconductors
- Nanoinclusions
- Thermal conductivity reduced from PbTe

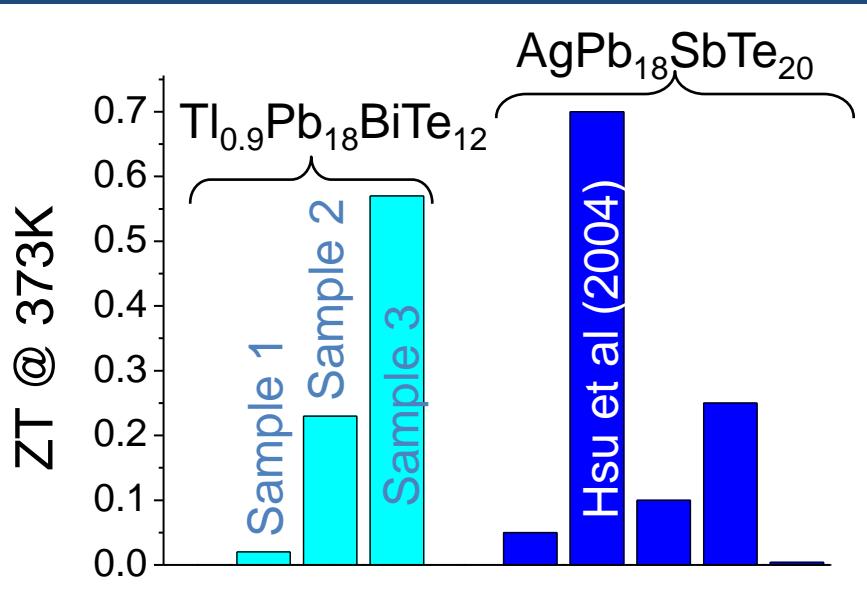
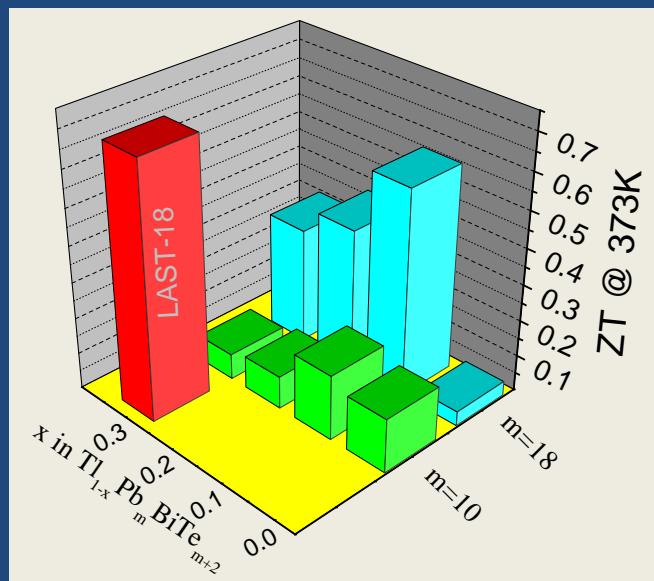
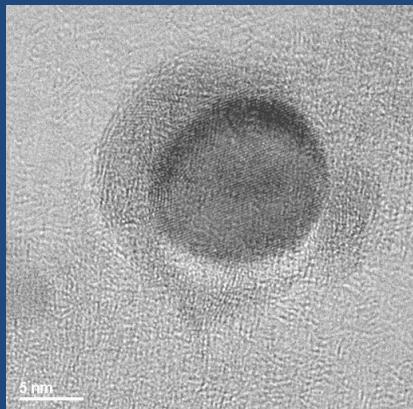
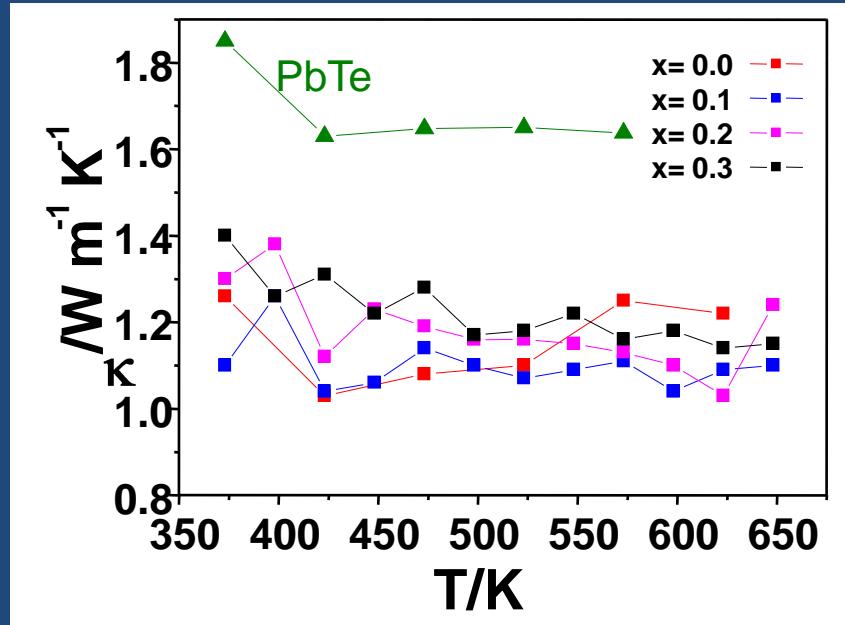
LAST=18

- *n*-type conduction
- $ZT_{max} = 2.2$  at 800K
- Silver deficient

Hsu et al, *Science*, **303**, 818, (2004)

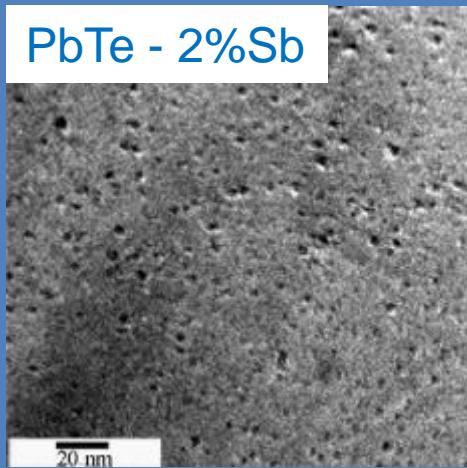
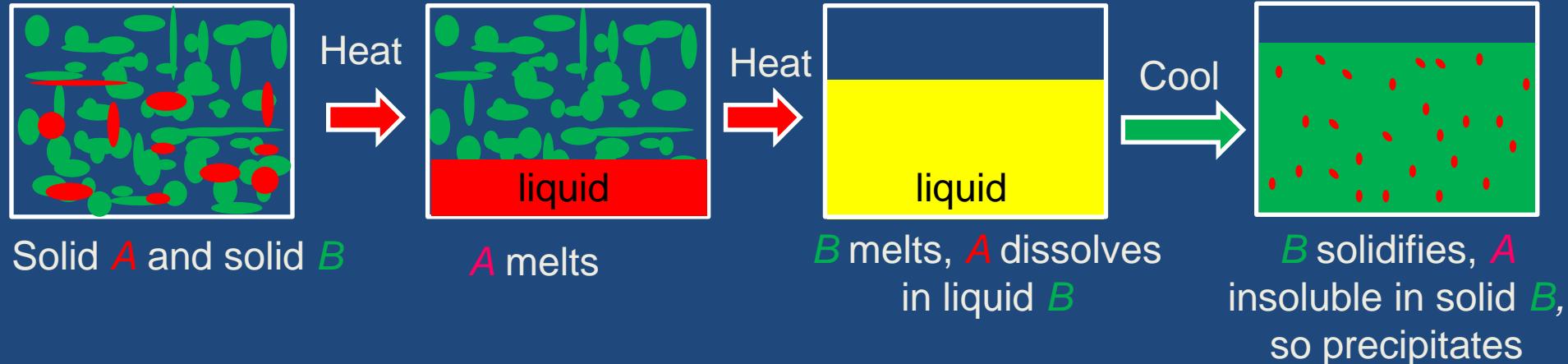
# $\text{Ti}_{1-x}\text{Pb}_m\text{BiTe}_{m+2}$

$\text{Ti}_{1-x}\text{Pb}_{18}\text{BiTe}_{20}$

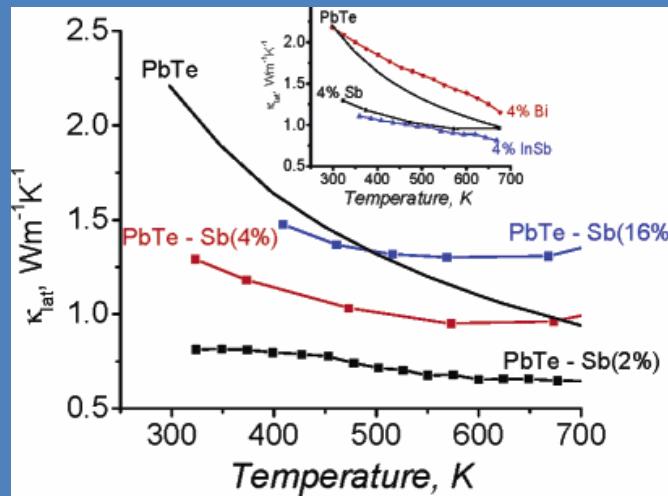


# Nanocomposite Materials

## Matrix Encapsulation



$$k_L = 0.8 \text{ W m}^{-1} \text{ K}^{-1}$$

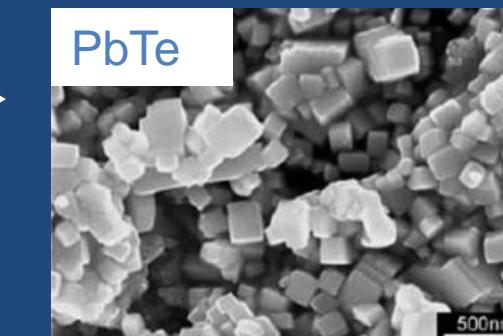
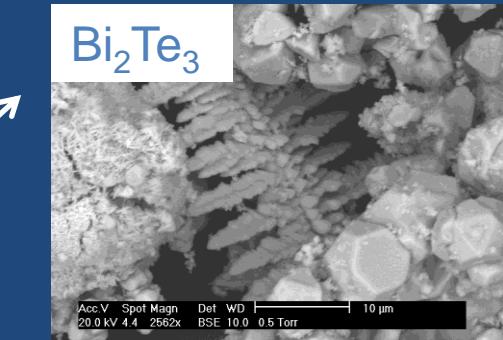


Sootsman *et al*, *Chem. Mater.*, **18**, 4994, (2006)

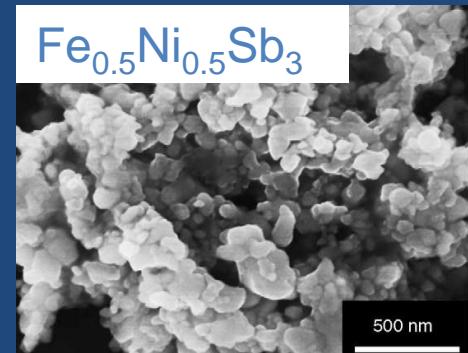
# Solvothermal Growth of Nanoparticulate Thermoelectrics

Metal Salts,  
Reducing agent  
Solvent,  
'Template  
Molecule'

$$\xrightarrow[T > T_{\text{b.p.}}]{P \leq 200 \text{ bar}}$$

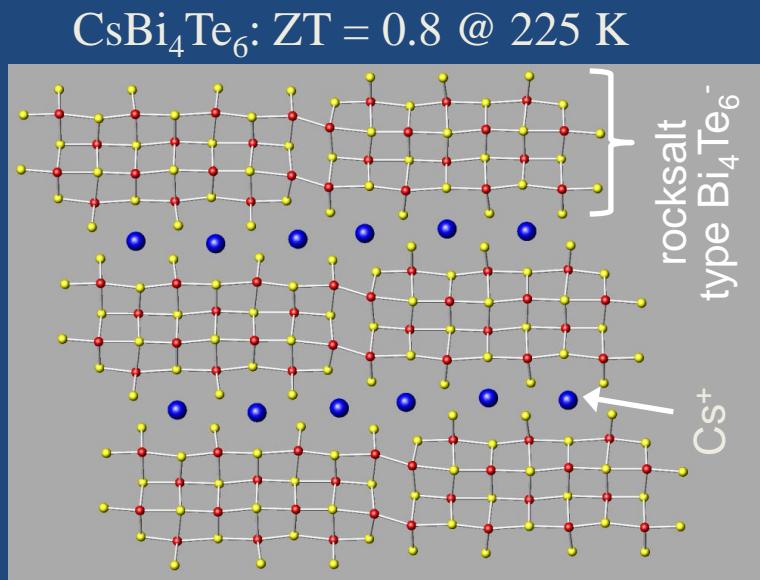
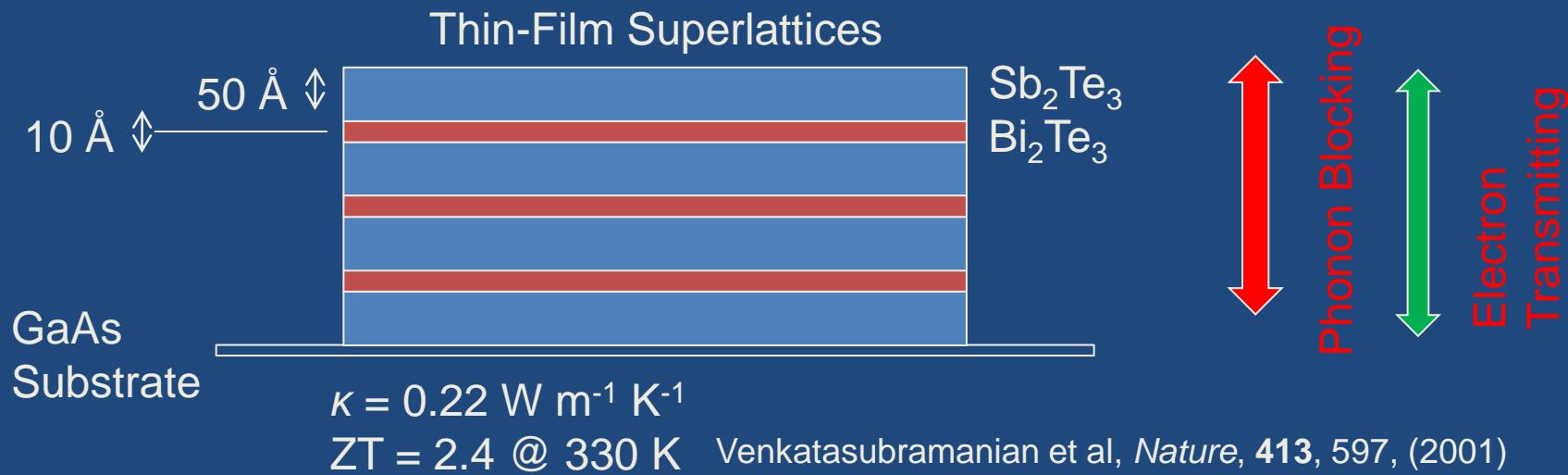


Ji et al. *J. Electron Mater.*, **36**, 271, (2007)



Mi et al. *JALCOM*, **399**, 260, (2005)

# Superlattices and Layered Materials

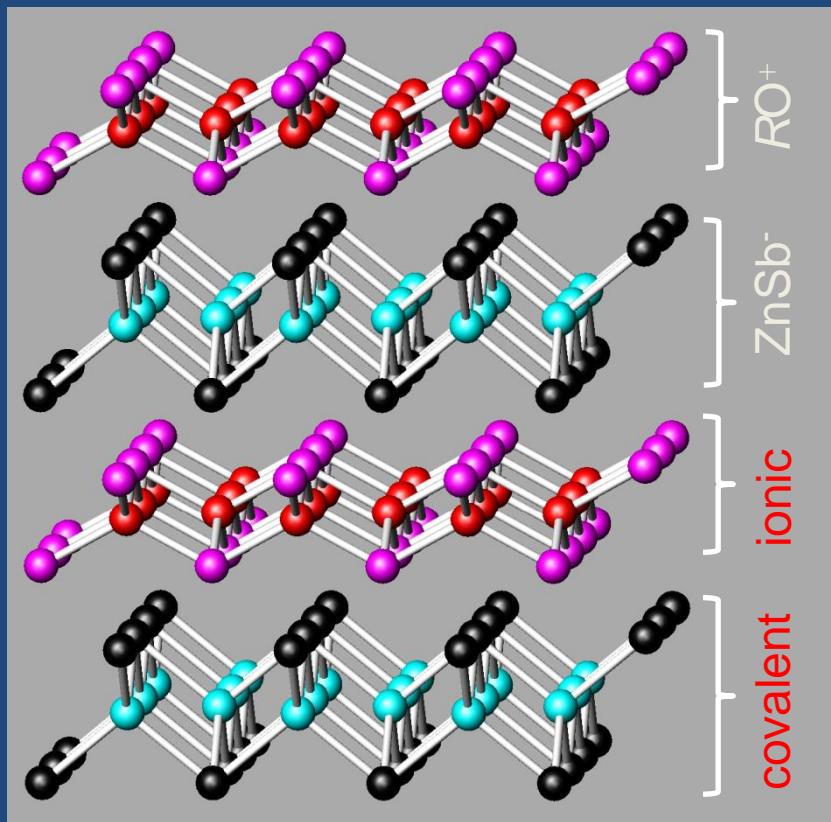


Chung et al, *JACS*, **126**, 6414, (2004)

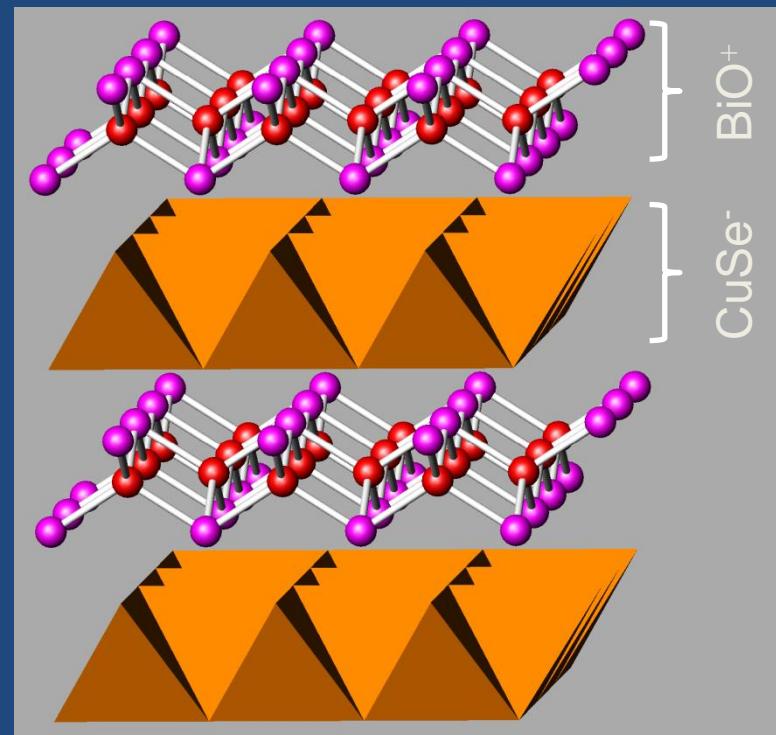
# Layered Materials



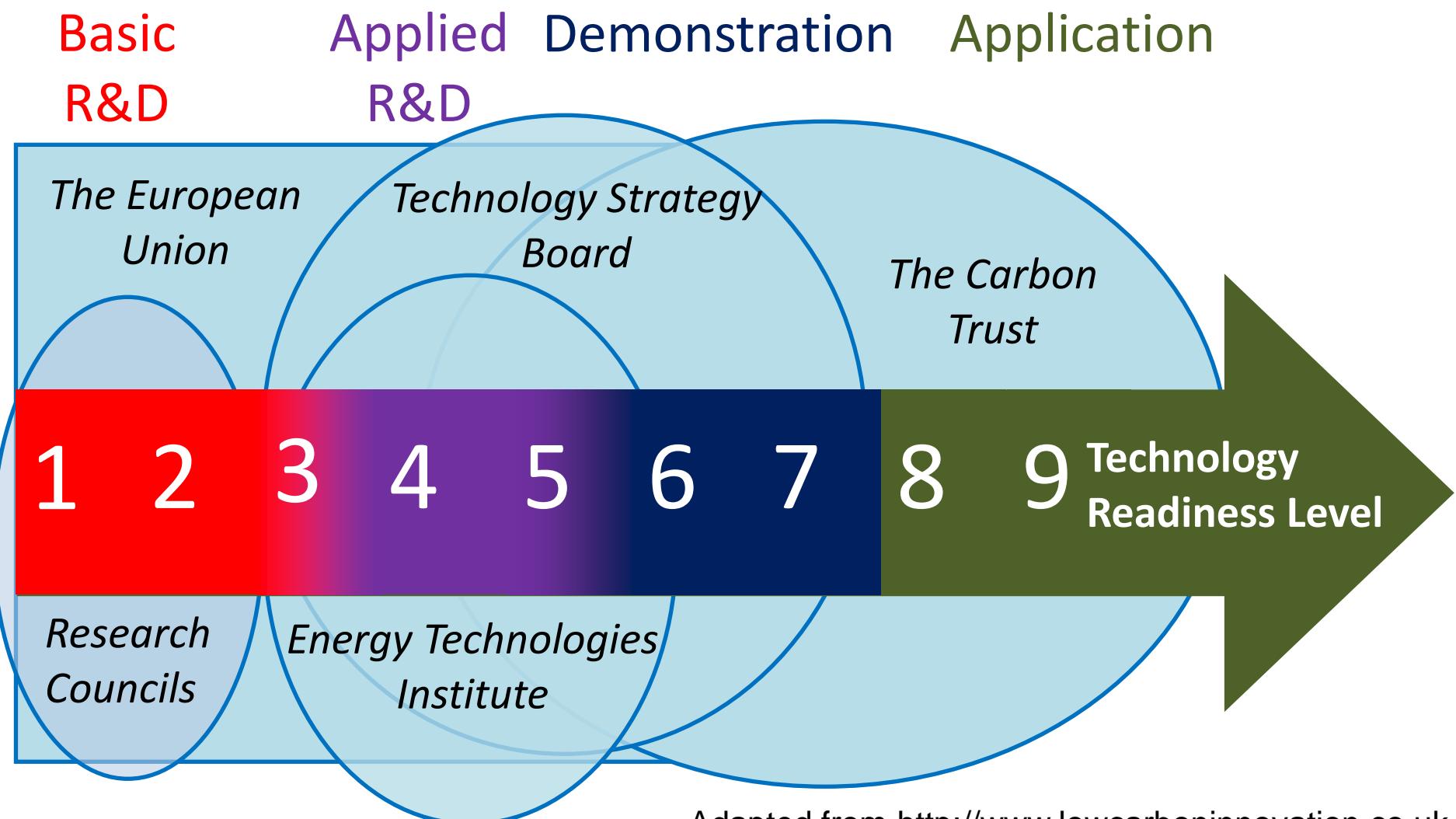
*ROZnSb*



*BiOCuSe*



# Pathways to Innovation



# Acknowledgements

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