University of Glasgow

Chemical Design and Synthesis of Chalcogenide Thermoelectrics

Duncan H. Gregory

UK Thermoelectric Network Meeting, Edinburgh. 14 Feb 2018

University of Glasgow

Chemical Design of Chalcogenide Thermoelectrics

1. Introduction

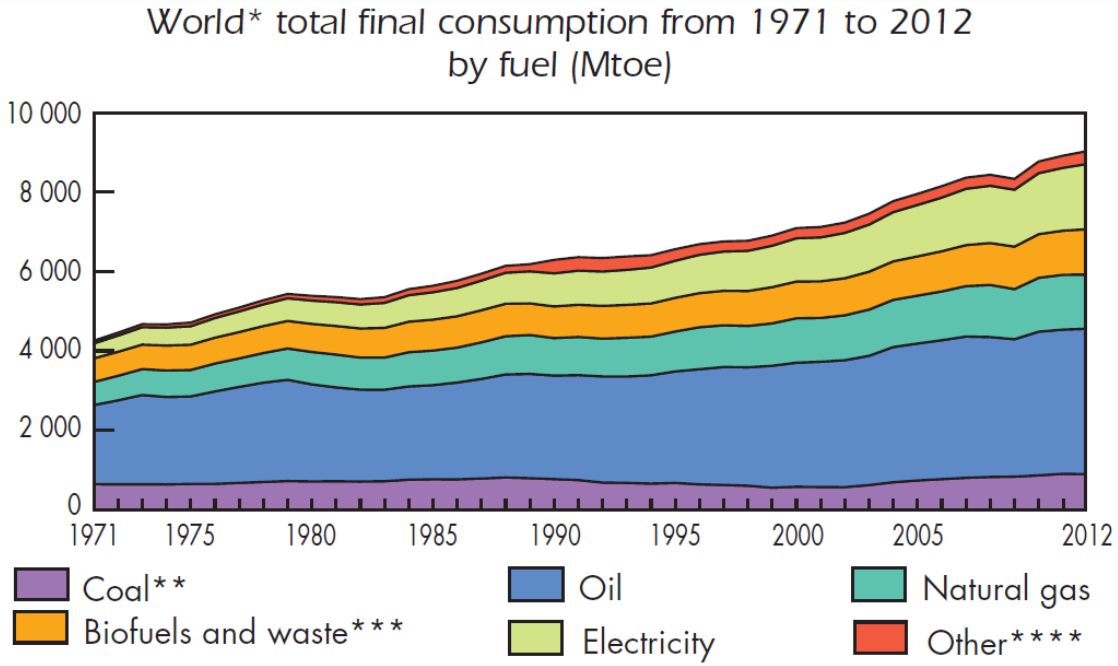
- The challenges
- Heat to power; thermoelectrics
- The state of the art

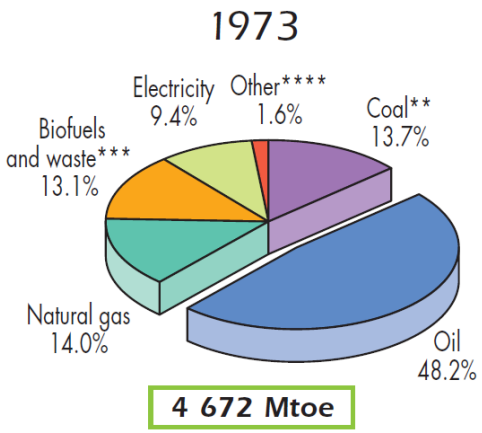
2. Chemically-designed chalcogenide thermoelectrics

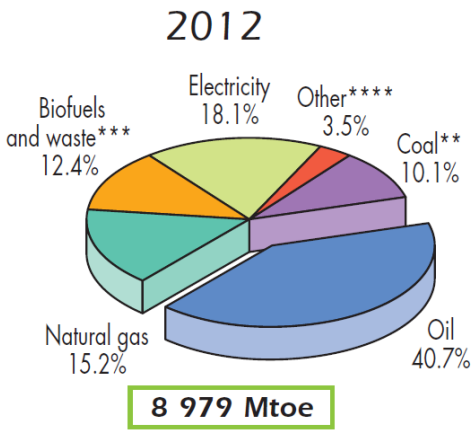
- Nanostructuring tin selenide, SnSe
- Modifying chalcogenide composition – SnTe and SnS
- Carrier doping in nano-tin chalcogenides

3. Summary

The challenges



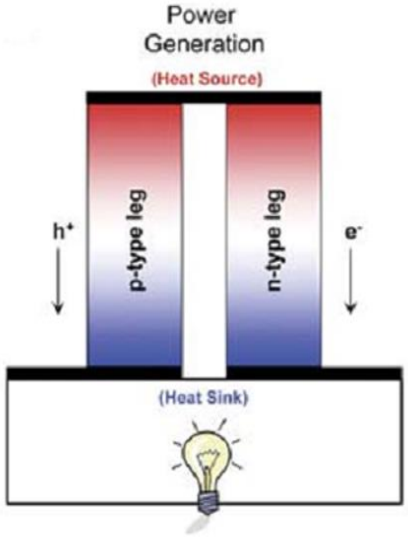




IEA Key World Energy Statistics, 2014

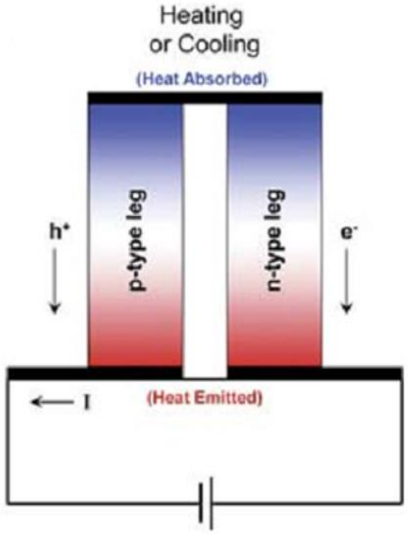
Heat to power; thermoelectrics

Seebeck Effect



Power generation mode

Peltier Effect



Thermoelectric cooling mode

Figure of Merit

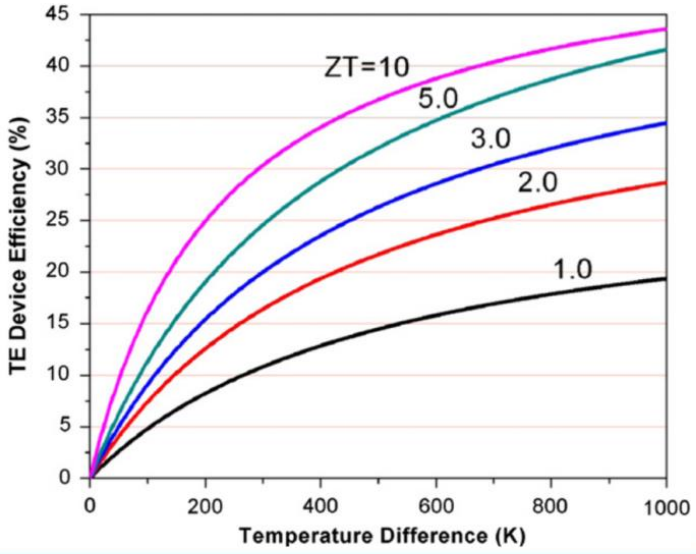
Seebeck coefficient

Electrical conductivity

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Temperature

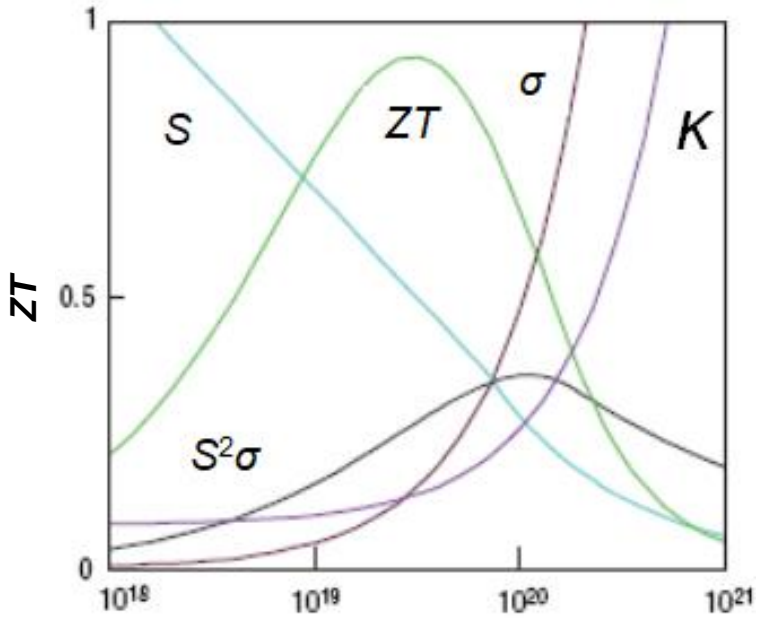
Thermal conductivity $\kappa_e + \kappa_L$



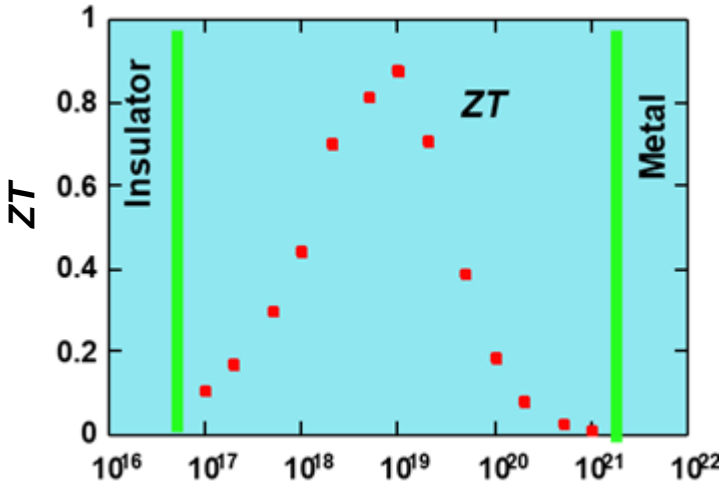
$$\text{Efficiency, } \eta = \frac{(T_h - T_c)(\gamma - 1)}{(T_c + \gamma T_h)} \qquad \gamma = \sqrt{1 + ZT}$$

J.R. Szczech, *et al. J. Mater. Chem.* 2011, **21**, 4037.

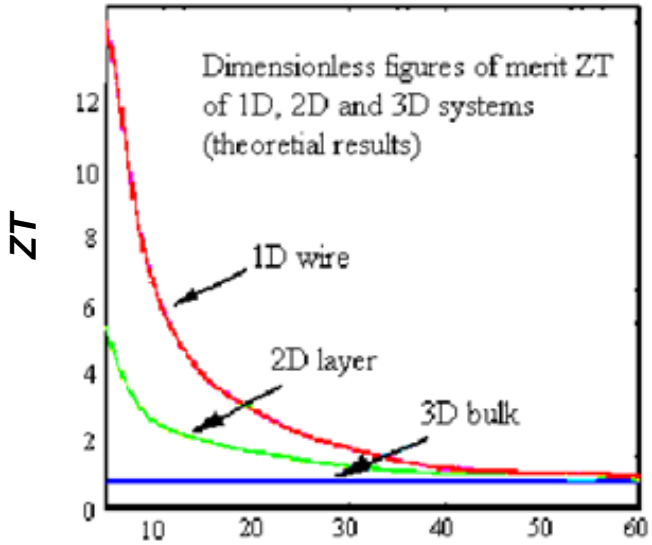
Heat to power; thermoelectrics



Carrier Concentration, n / cm^{-3}



n / cm^{-3}

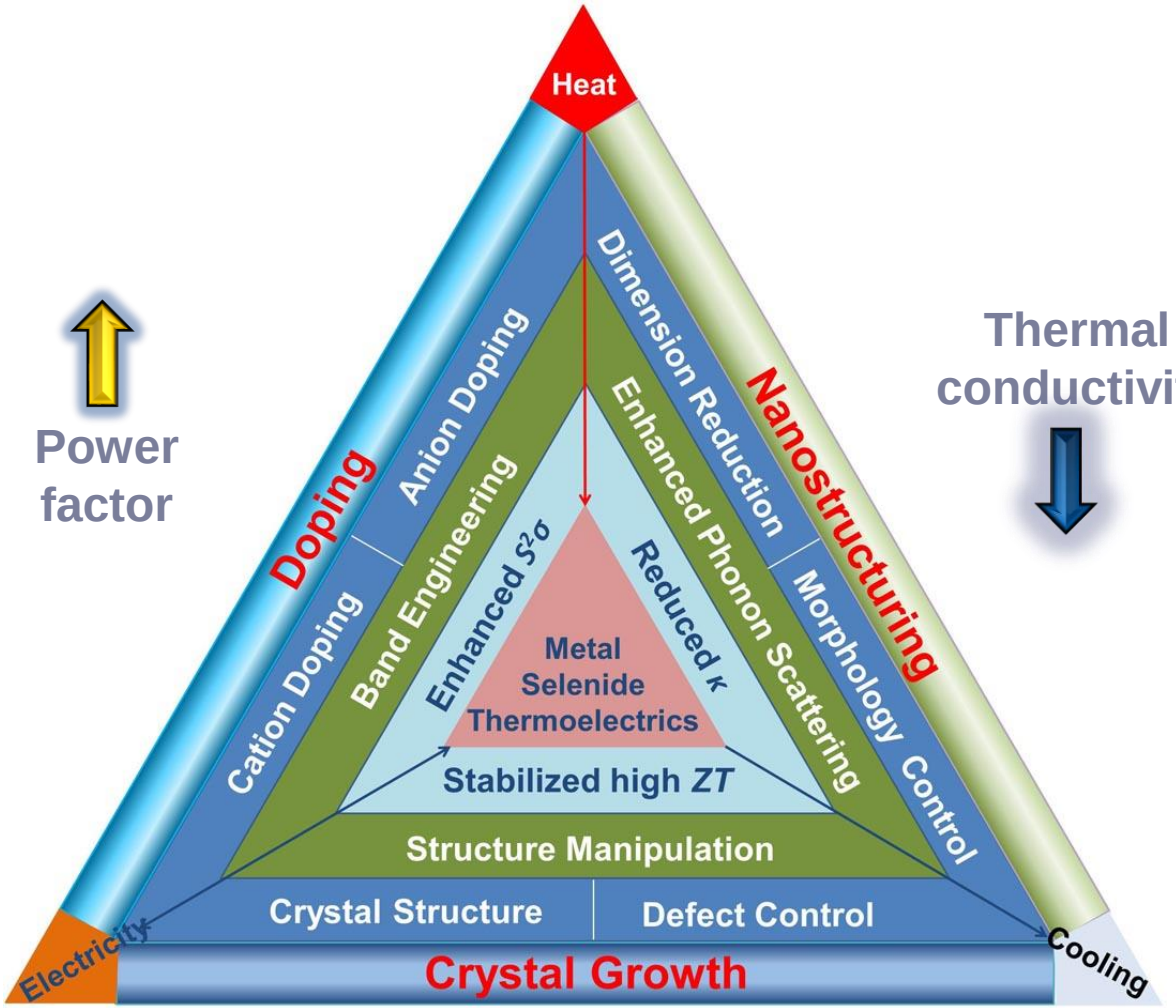


Layer thickness (2D) or wire diameter (1D) / Å

Snyder and Toberer, *Nature Mater*., 2008, **7**, 105.

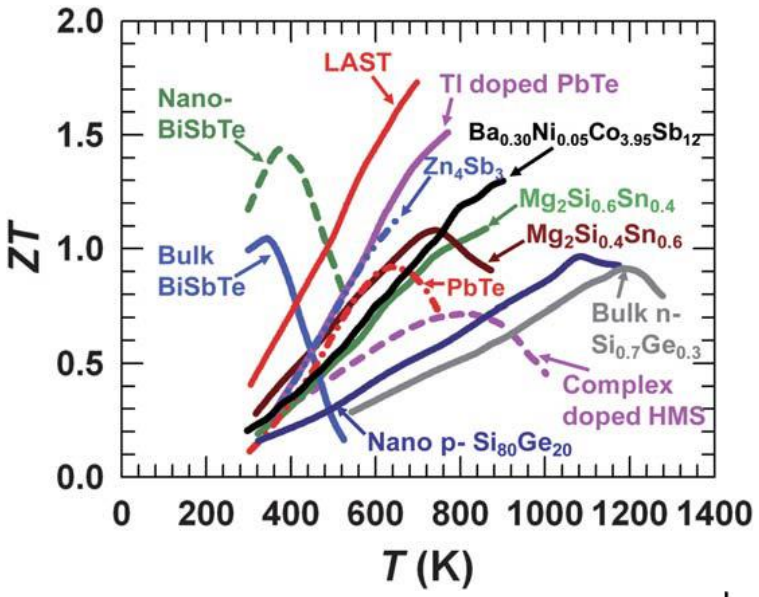
X. Sun *et al Appl. Phys.Lett*. 1999, **74,** 4005

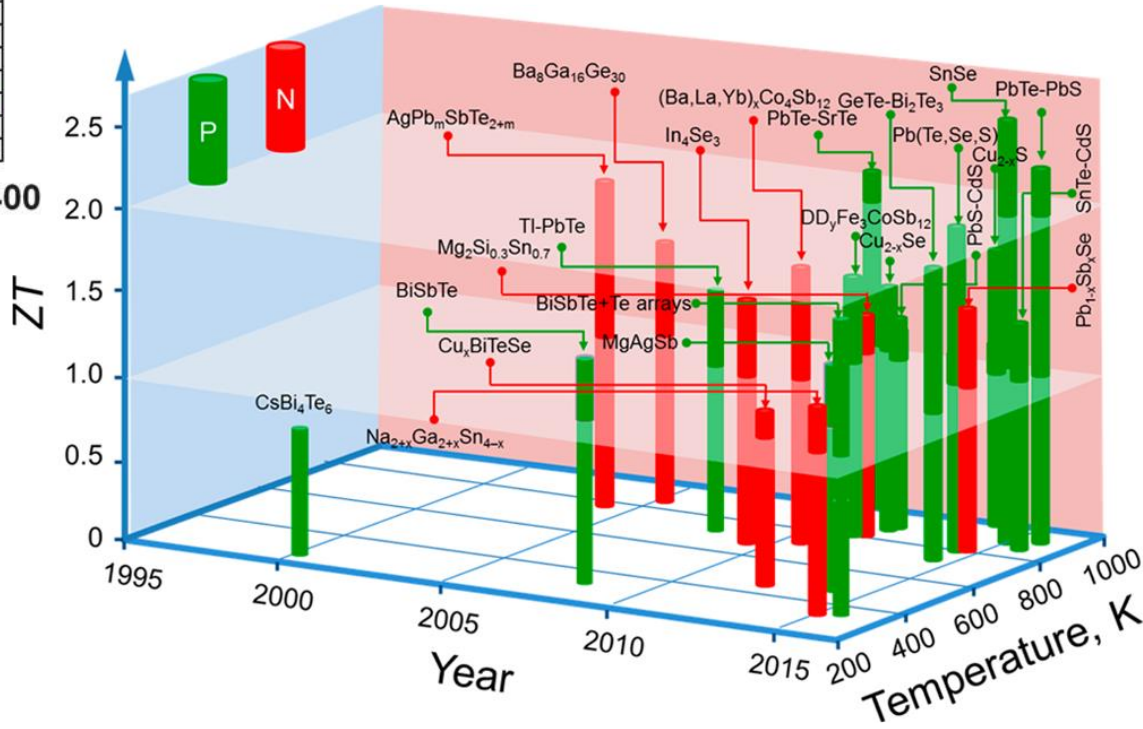
Heat to power; thermoelectrics



Adapted from G. Han, *et al. Small*, 2014, **10**, 2747.

The state of the art



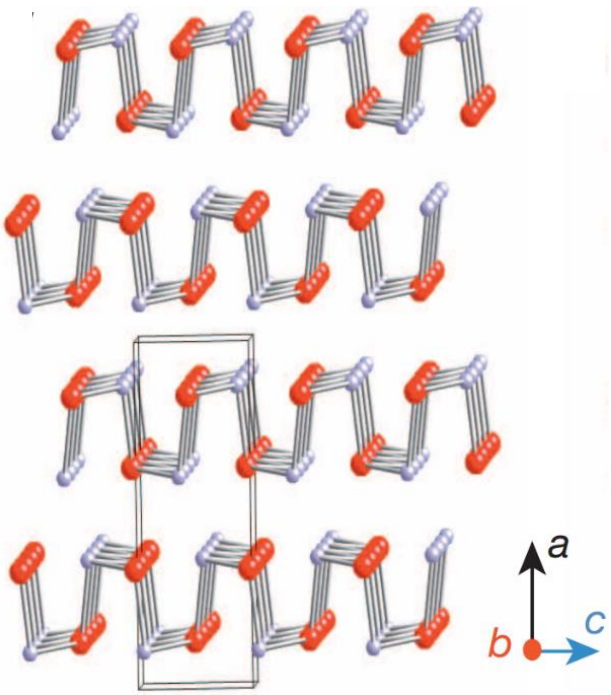


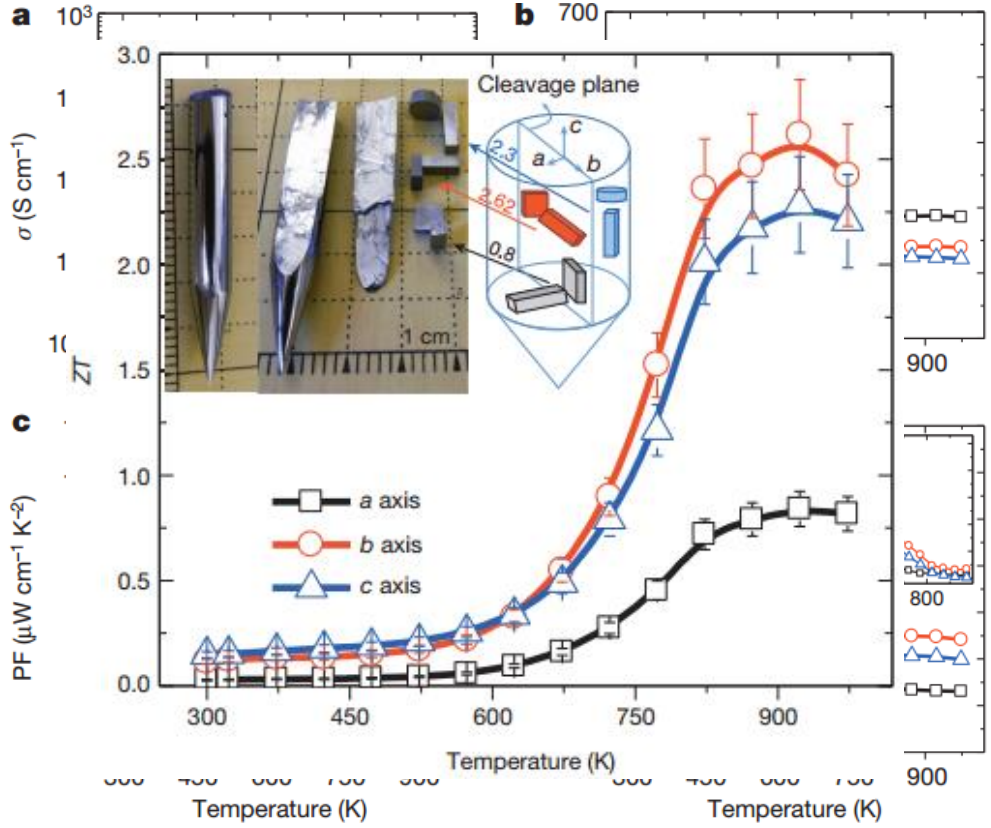
J.R. Szczech, *et al. J. Mater. Chem.* 2011, **21**, 4037.

Tan, Zhao and Kanatzidis, *Chem. Rev.* 2016, **116**, 12123

The state of the art

SnSe Orthorhombic, space group *Pnma*
a = 11.5156(5) Å, *b* = 4.1571(2) Å, *c* = 4.4302(3) Å



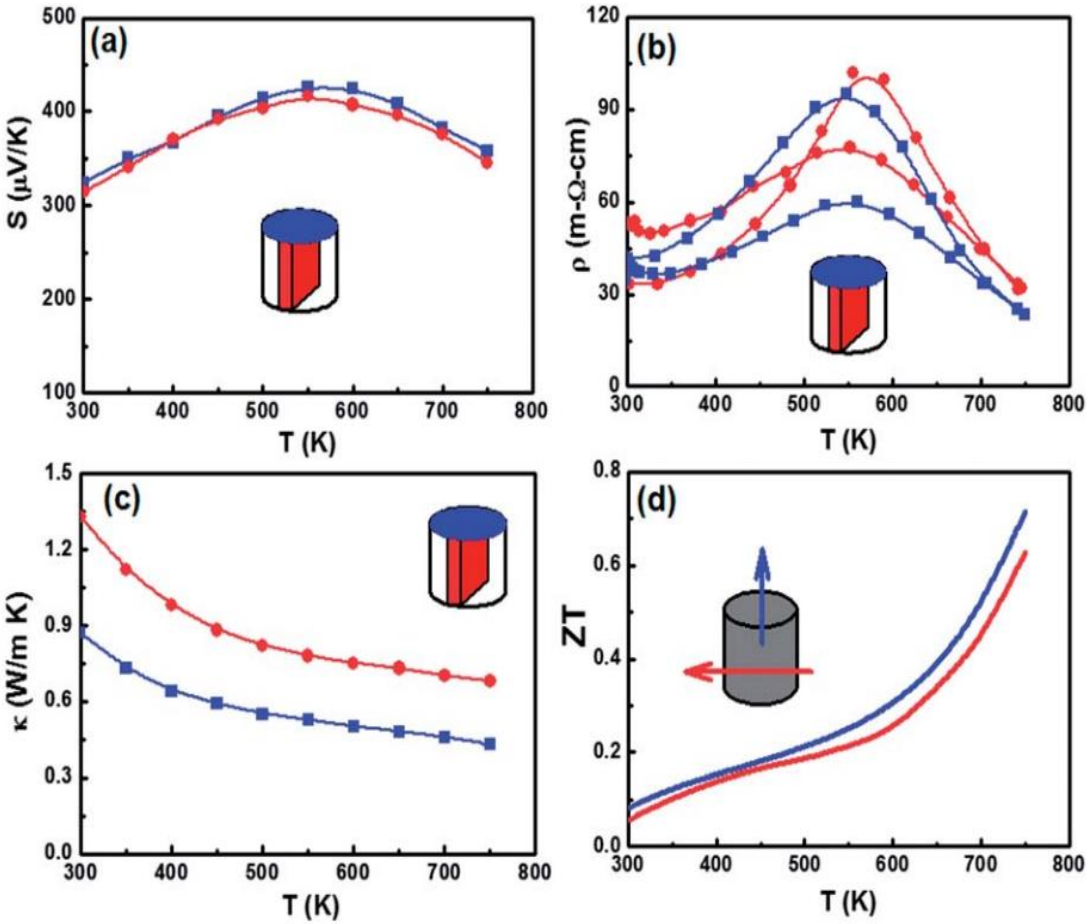


Anisotropic properties:
Optimum TE performance

L.-D. Zhao, *et al, Nature,* 2014, **508**, 373 .

The state of the art

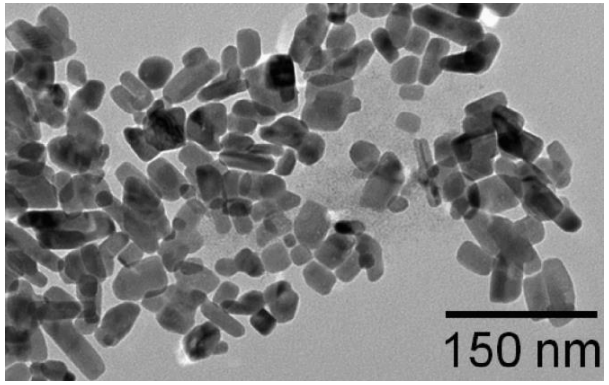
Polycrystalline materials:



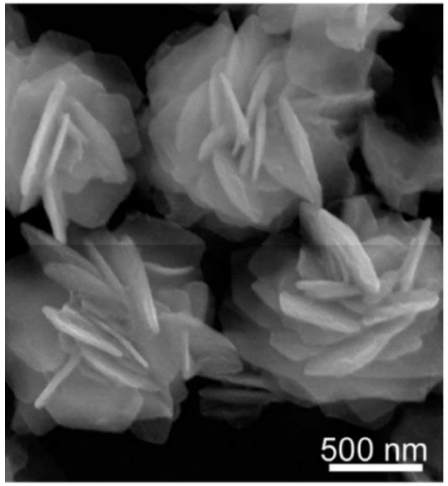
- *Time-consuming synthesis*
- *Anisotropic performance*
- *Higher thermal conductivity*

C.-L. Chen *et al J. Mater. Chem. A* 2014, **2**, 11171.

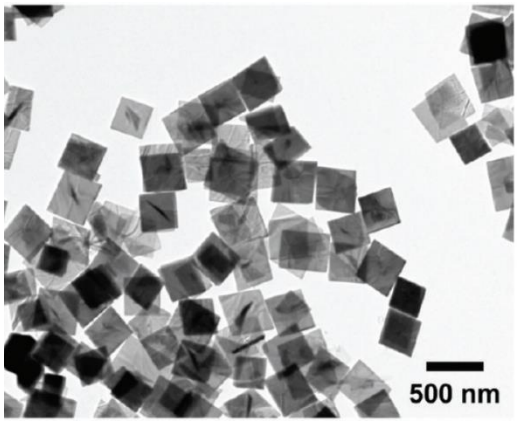
The state of the art



$SnCl_2$+di-tert-butyl diselenide in dodecylamine + dodecanethiol



$SnCl_2$+ trioctylphosphine selenide TOP-Se in oleylamine + hexamethyldisilazane



$SnCl_4 \cdot 5H_2O$ + SeO_2 in oleylamine

- Limited scale synthesis
- Surfactants - impurities at nanoparticle surfaces; reduced σ
- Control of doping difficult.

M.A. Franzman, *et al, JACS*, 2010, **132**, 4060. D.D. Vaughn II, *et al., ACS Nano,* 2011, **5**, 8852. L. Li, *et al., JACS,* 2013, **135**, 1213.

University of Glasgow

Chemical Design of Chalcogenide Thermoelectrics

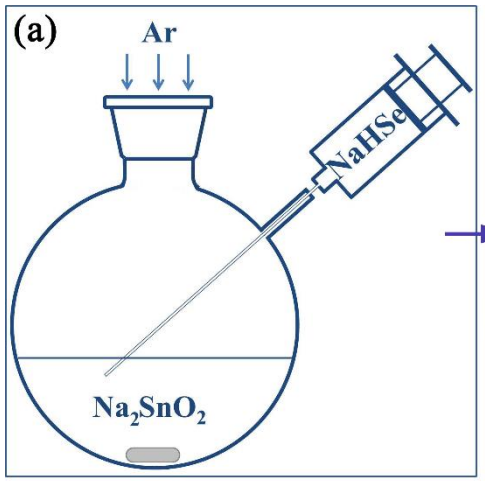
1. Introduction
   - The challenges
   - Heat to power; thermoelectrics
   - The state of the art

2. Chemically-designed chalcogenide thermoelectrics
   - Nanostructuring tin selenide, SnSe
   - Modifying chalcogenide composition – SnTe and SnS
   - Carrier doping in nano-tin chalcogenides

3. Summary

Nano structuring tin selenide, SnSe

$$Na_2SnO_2 + NaHSe + H_2O \rightarrow 3\ SnSe + 3\ NaOH$$

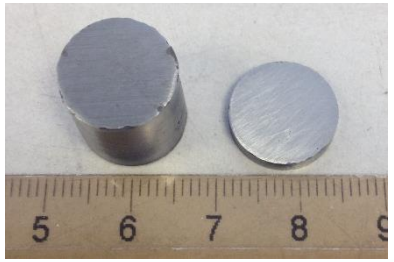


Materials Design and Synthesis

- *Surfactant free*
- *Effective morphology control*
- *Large-scale solution synthesis*
- *Fast Synthesis*
- *Cheap and environmentally friendly precursors*

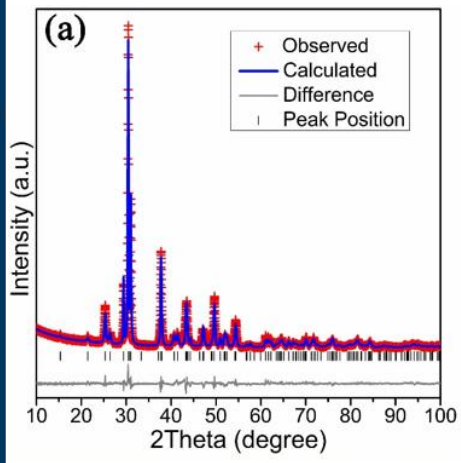
Thermoelectric Performance

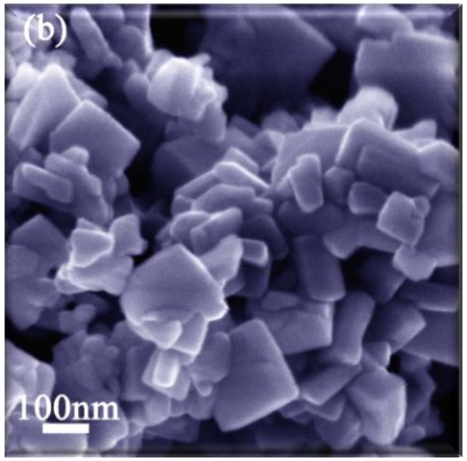
- *Enhanced power factor*
- *Tuneable conducting behaviour (e.g p-/n-type)*

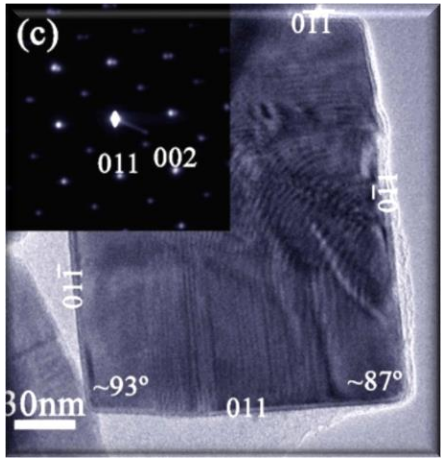


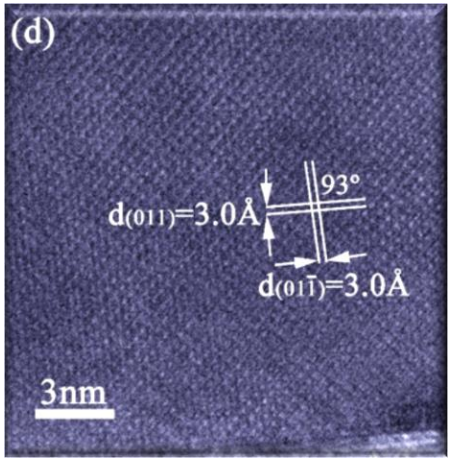
Angew. Chem. Int. Ed., 2016, **55**, 6433-6437

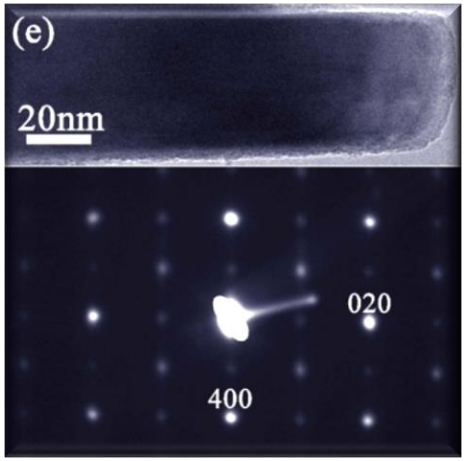
Nano structuring tin selenide, SnSe

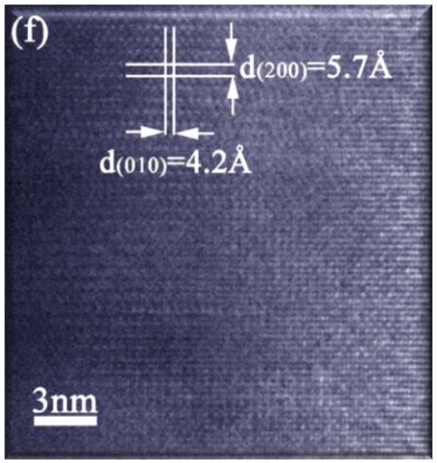


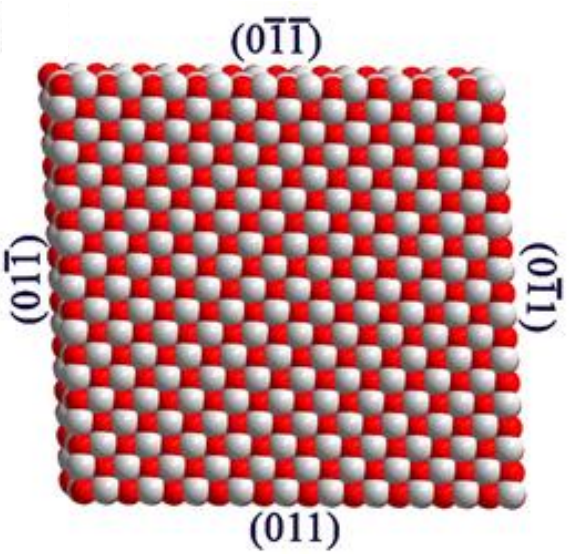






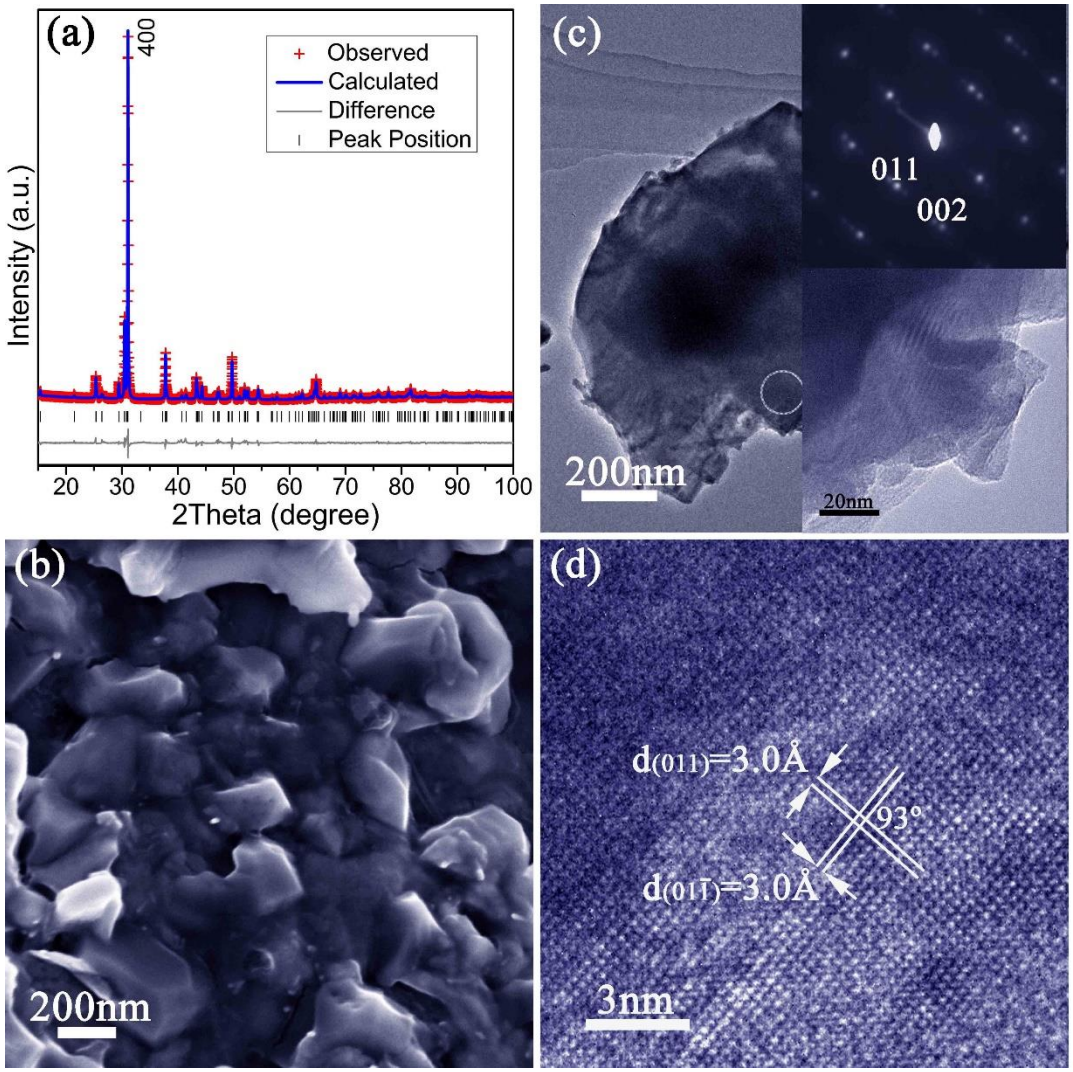






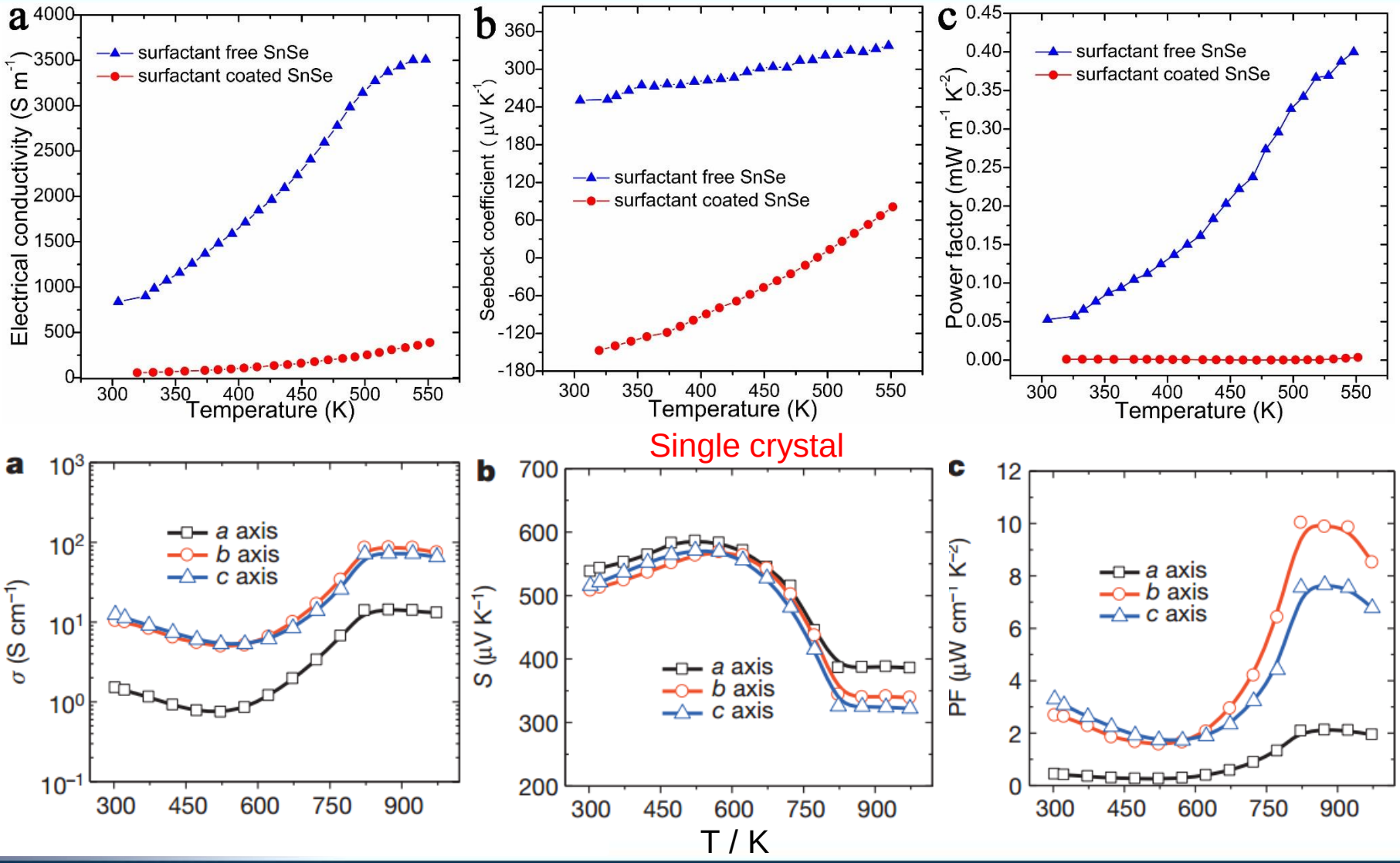
Angew. Chem. Int. Ed., 2016, **55**, 6433-6437

Nano structuring tin selenide, SnSe



Angew. Chem. Int. Ed., 2016, **55**, 6433-6437

Nano structuring tin selenide, SnSe



Angew. Chem. Int. Ed., 2016, **55**, 6433-6437

L.-D. Zhao, *et al*, *Nature*, 2014, **508**, 373 .

Chemical Design of Chalcogenide Thermoelectrics

1. Introduction

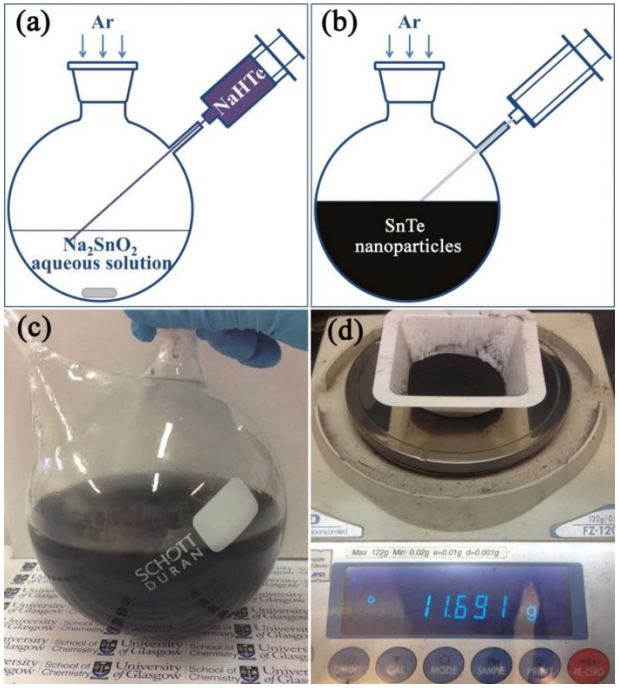
- The challenges
- Heat to power; thermoelectrics
- The state of the art

2. Chemically-designed chalcogenide thermoelectrics

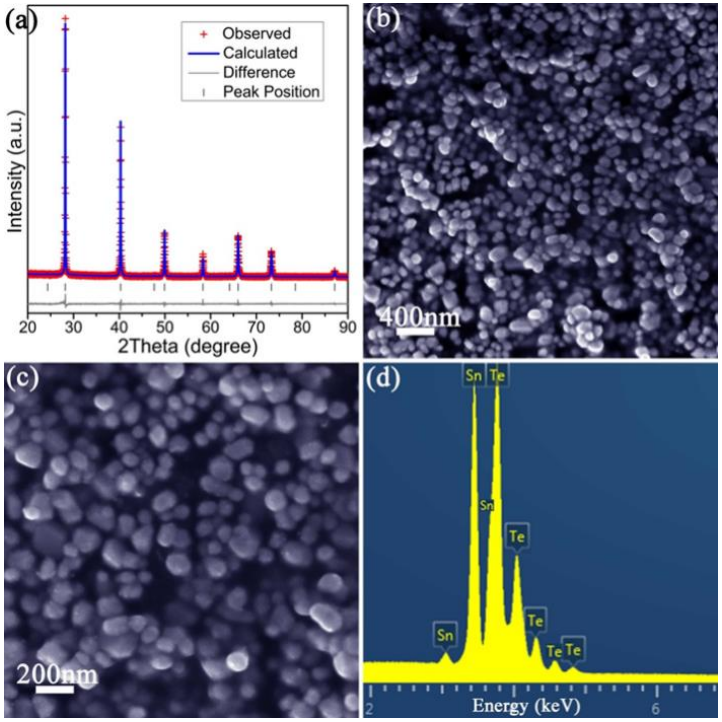
- Nanostructuring tin selenide, SnSe
- Modifying chalcogenide composition – nano-SnTe and nano-SnS
- Carrier doping in nano-tin chalcogenides

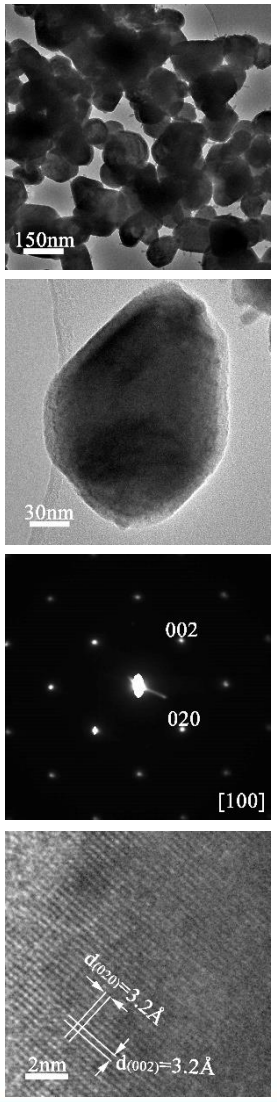
3. Summary

Modifying chalcogenide composition



Cubic, *Fm*3*m;*
a = 6.3234(1)
NaCl-type





$Na_2SnO_2 + NaHTe + H_2O$

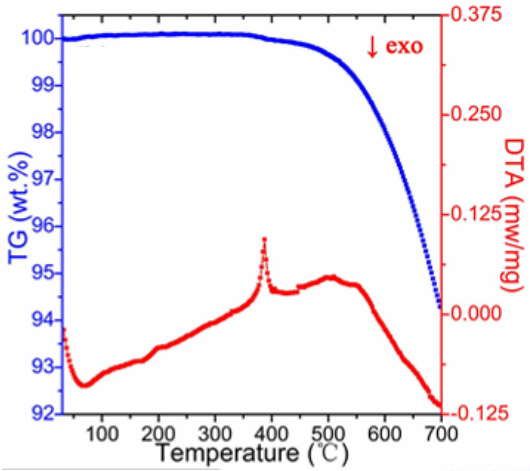
↓

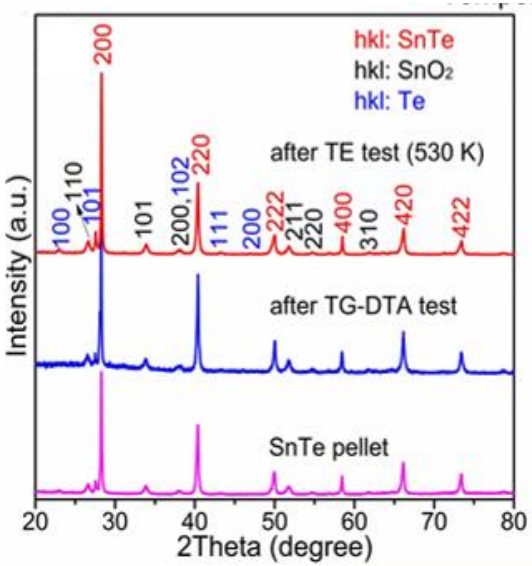
$3\ SnTe + 3\ NaOH$

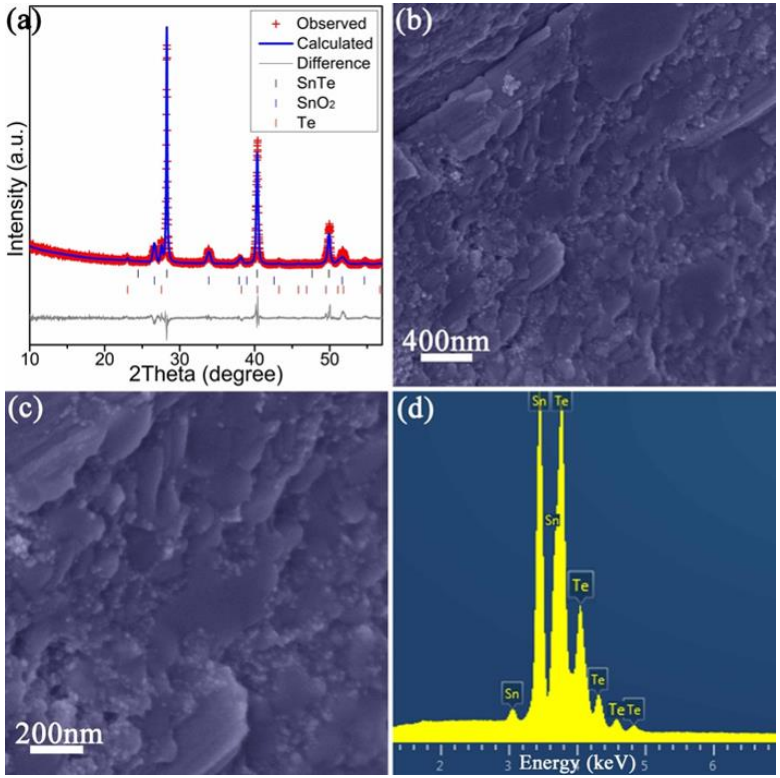
Materials, 2017, **10**, 233*; DOI:10.3390/ma10030233*

Modifying chalcogenide composition

Thermally stable ≤ 750 K



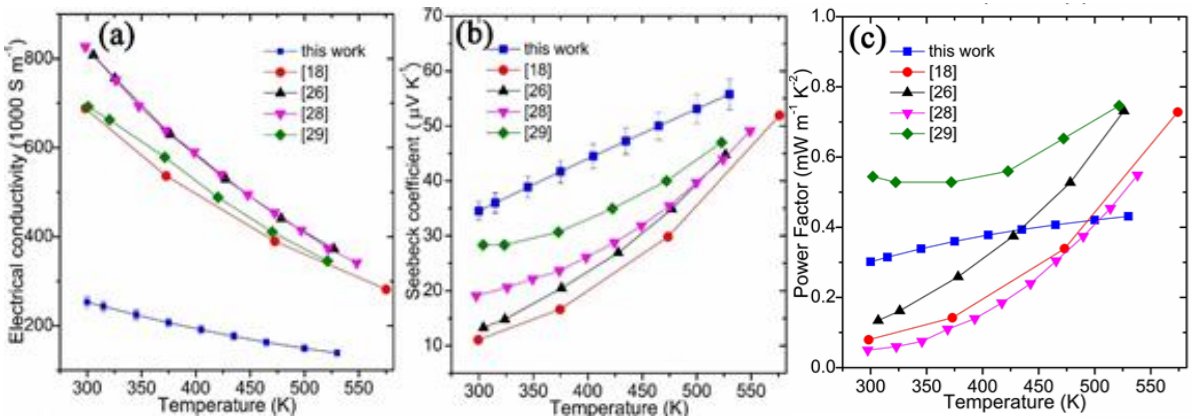


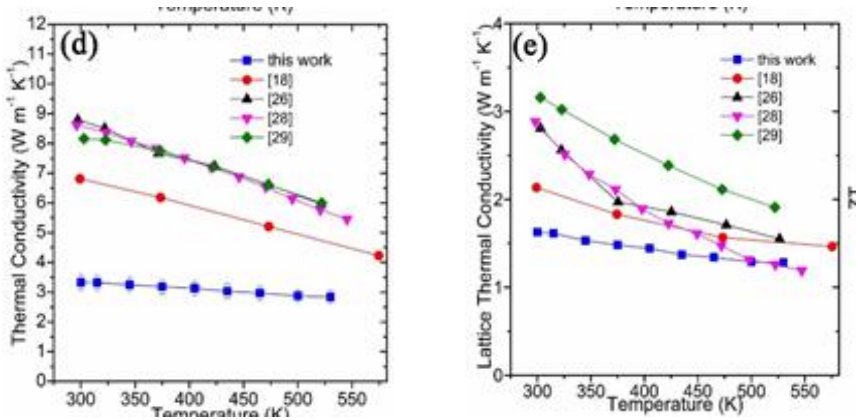


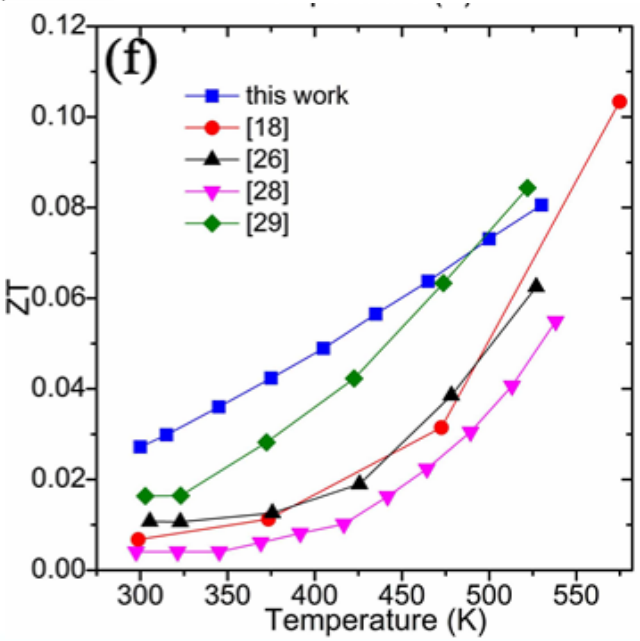
Spark Plasma Sintered (SPS) pellets;
723 K; 50 GPa

Materials, 2017, **10**, 233; *DOI:10.3390/ma10030233*

Modifying chalcogenide composition





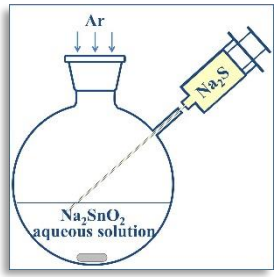


Improved values of S and κ but reduced σ *cf*. other SnTe. Likely due to SnO_2 from SPS.

Materials, 2017, **10**, 233; *DOI:10.3390/ma10030233*

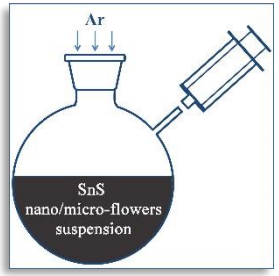
Modifying chalcogenide composition

1 **SnS Nanoparticle Synthesis:**

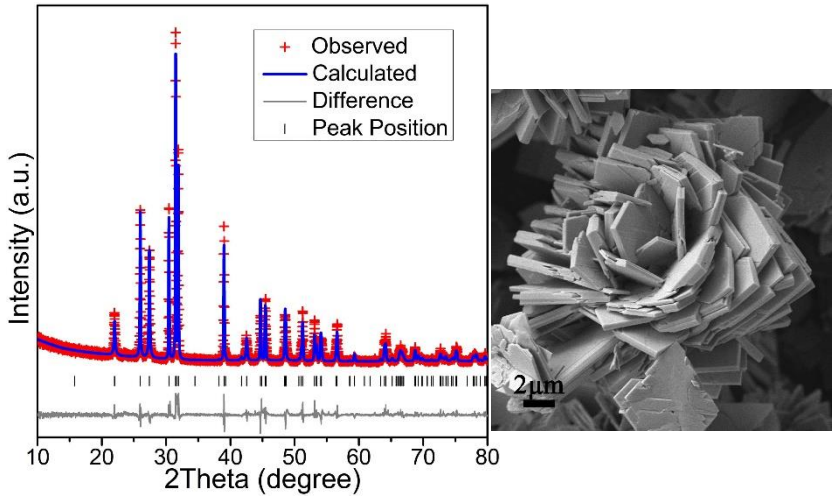


$$Na_2S + Na_2SnO_2 + 2\,H_2O \rightarrow SnS + 4\,NaOH$$

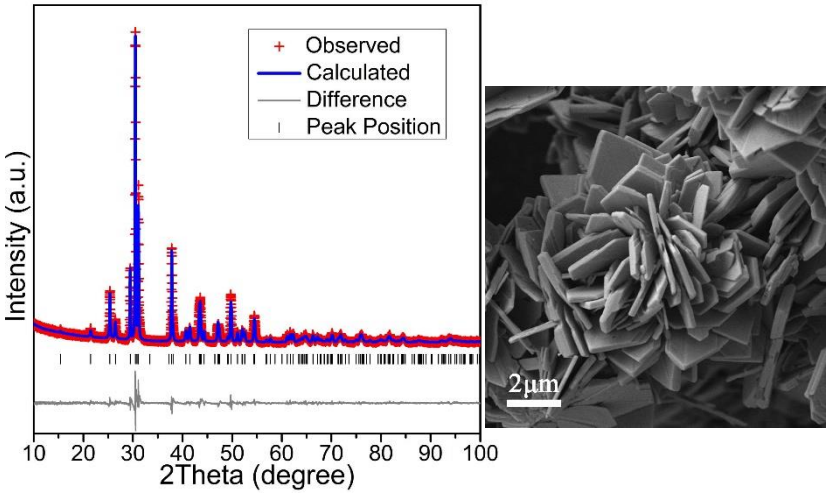
2 **Topotactic anion exchange to Sn(S,Se):**



$$SnS + x\,NaHSe + x\,NaOH \rightarrow SnS_{1-x}Se_x + x\,Na_2S + x\,H_2O$$



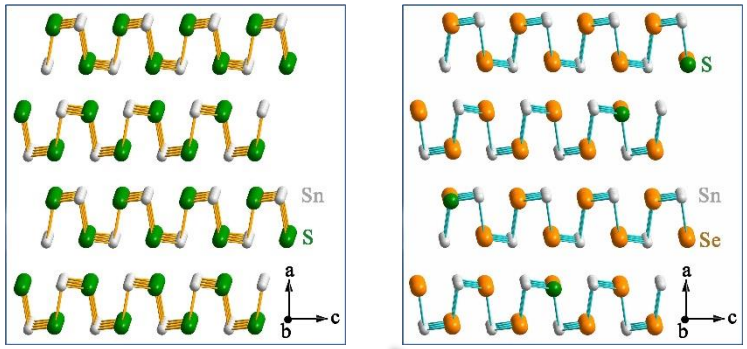
SnS



$SnS_{1-x}Se_x$

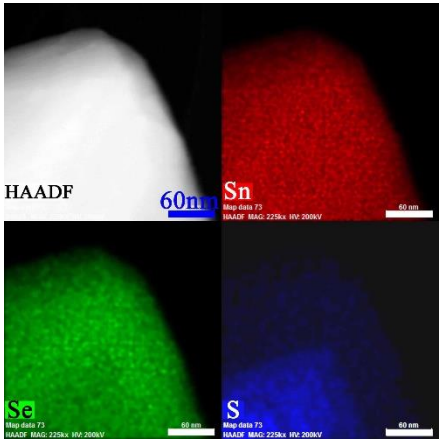
Chem. Sci. 2018, *under revision*

Modifying chalcogenide composition

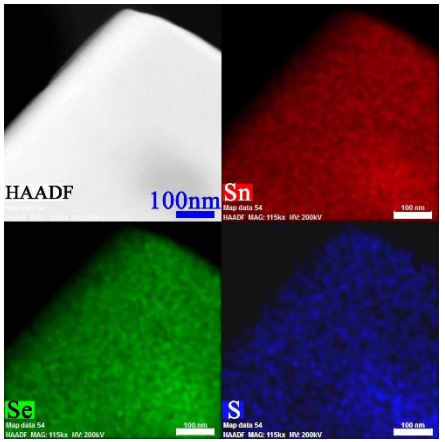


SnS → $SnS_{0.1}Se_{0.9}$

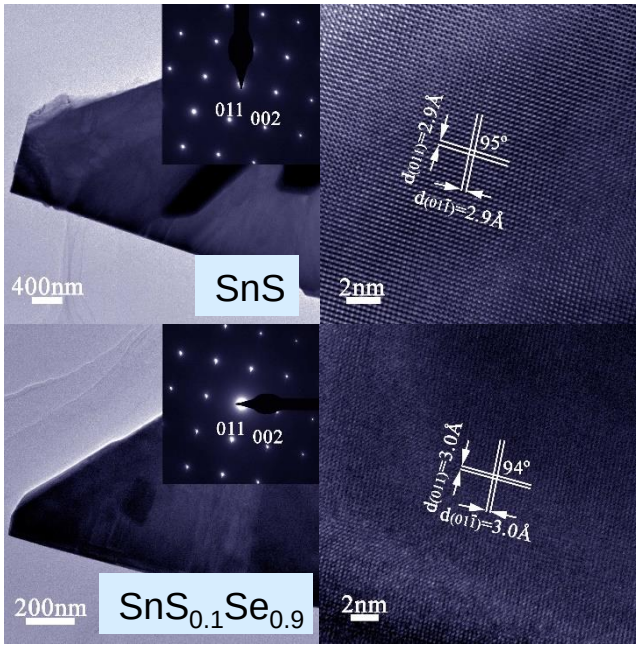
High Angle Annular Dark Field (HAADF) imaging

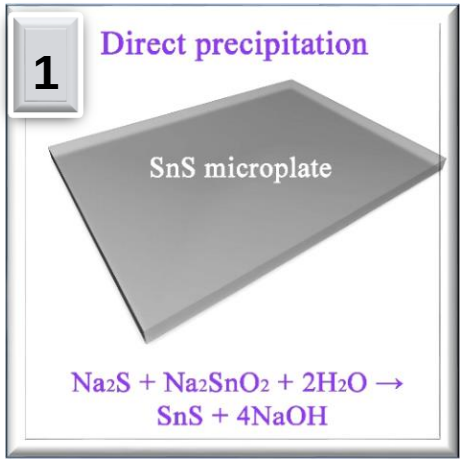


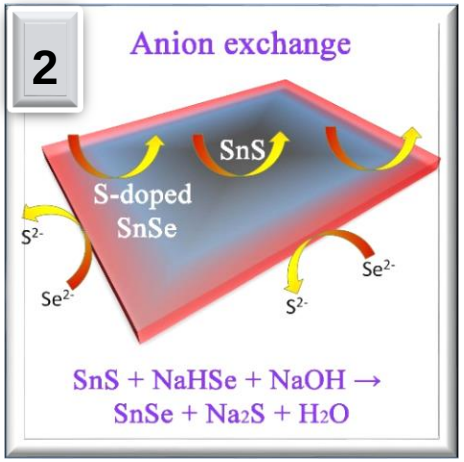
1 min anion exchange



2 h anion exchange





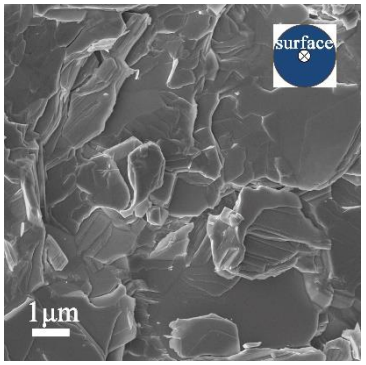


Chem. Sci. 2018, *under revision*

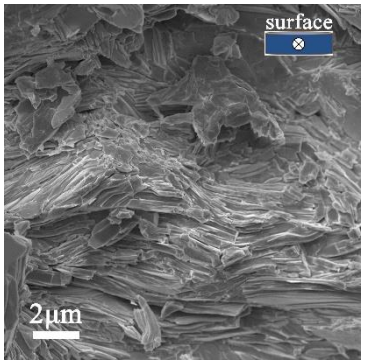
Modifying chalcogenide composition

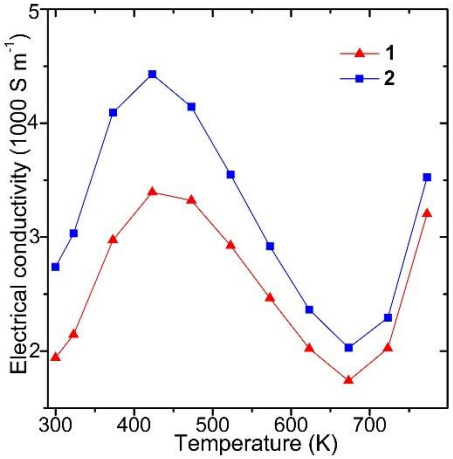
SPS pressed pellets:

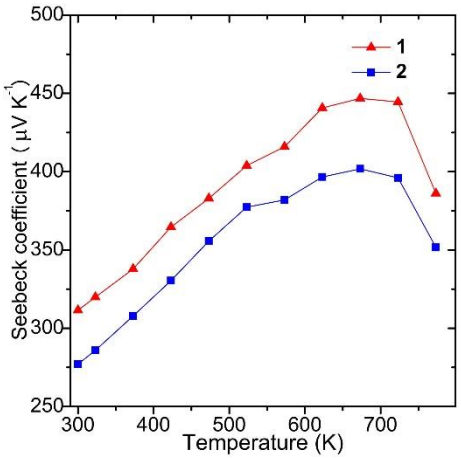
Pellet face, ⊥ pressing direction

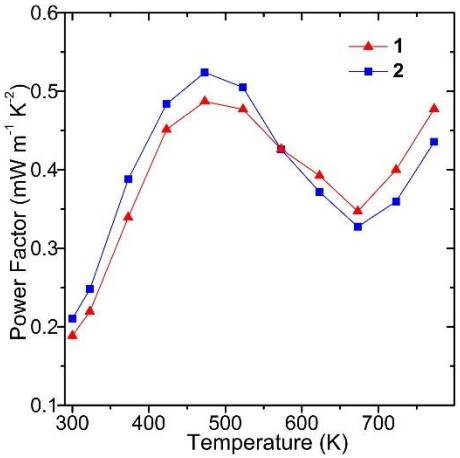


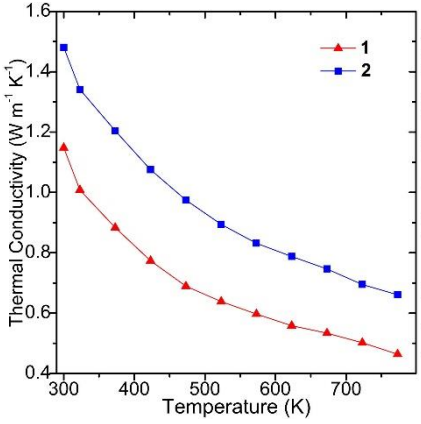
Pellet edge, ∥ pressing direction

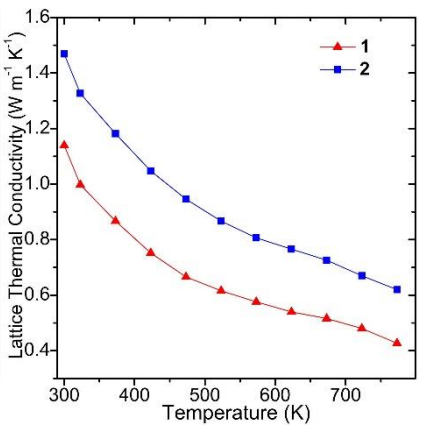


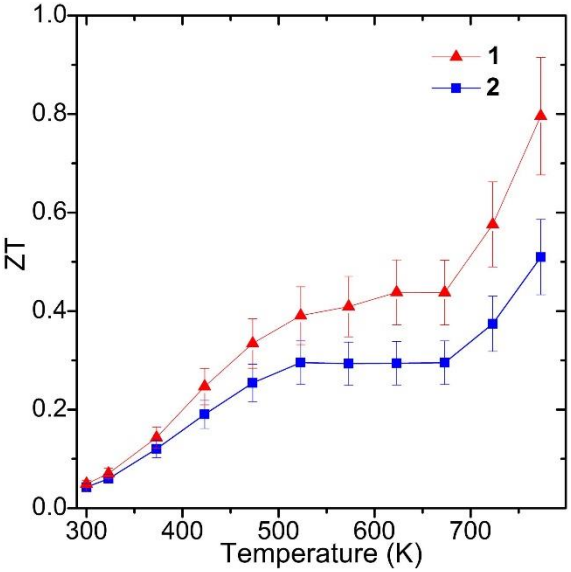












Chem. Sci. 2018, *under revision*

University of Glasgow

Chemical Design of Chalcogenide Thermoelectrics

1. Introduction

- The challenges
- Heat to power; thermoelectrics
- The state of the art

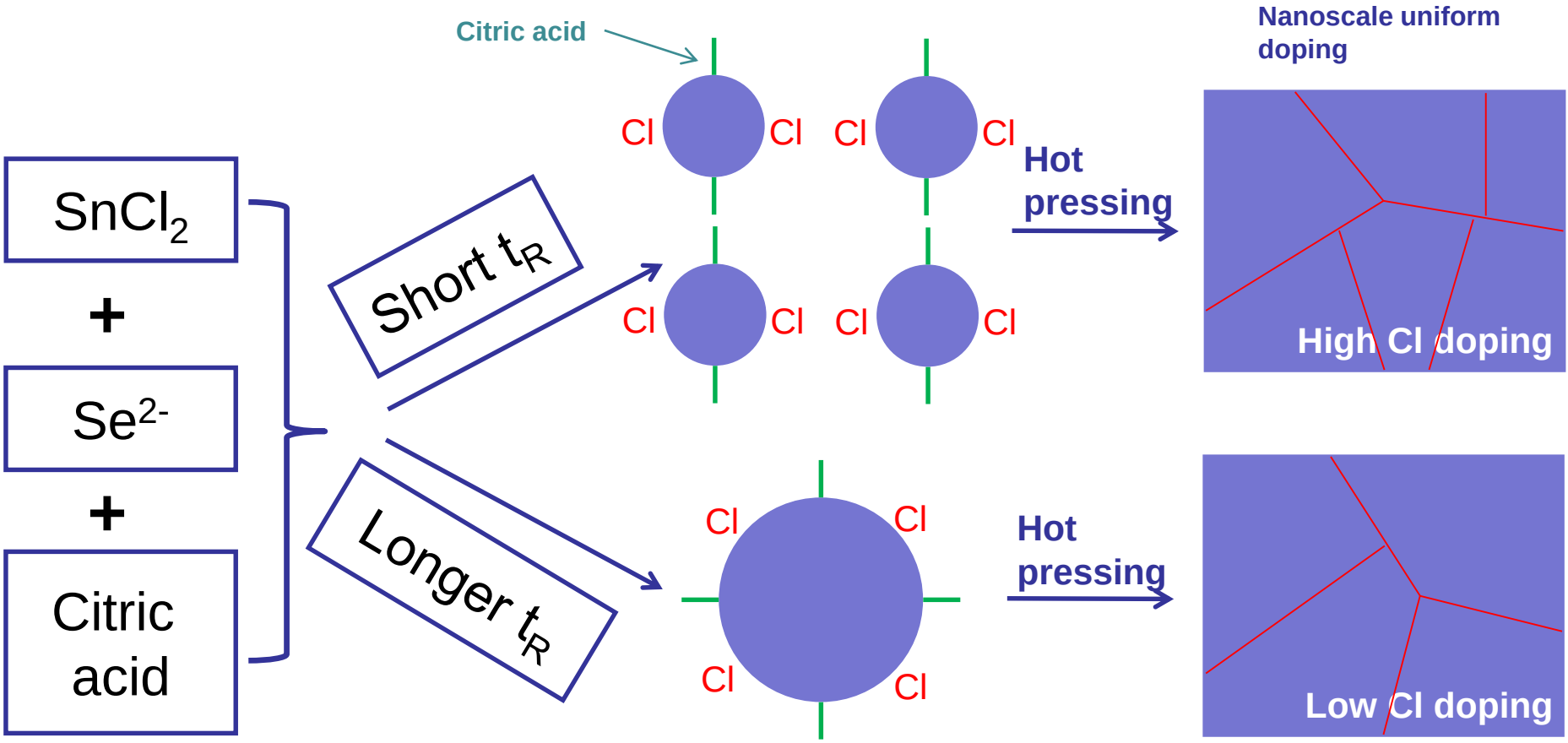
2. Chemically-designed chalcogenide thermoelectrics

- Nanostructuring tin selenide, SnSe
- Modifying chalcogenide composition – SnTe and SnS
- Carrier doping in nano-tin chalcogenides

3. Summary

Carrier doping in nano-tin chalcogenides

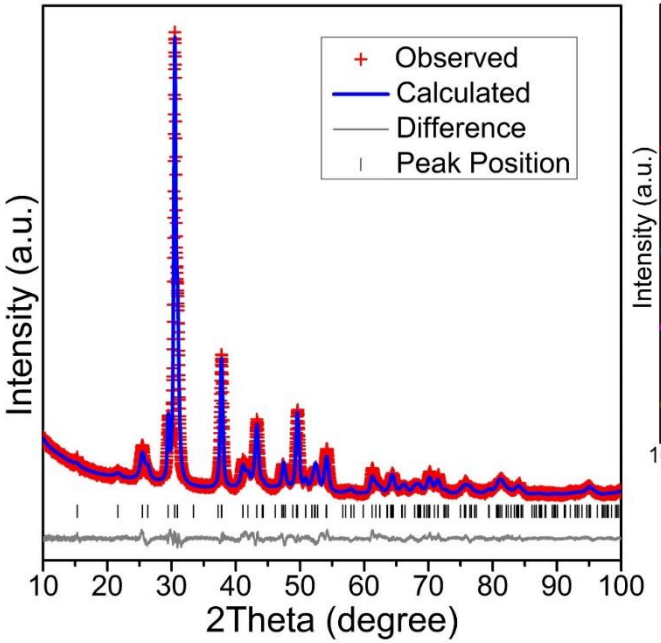
In-situ surfactant replacement strategy in SnSe nanoparticles:

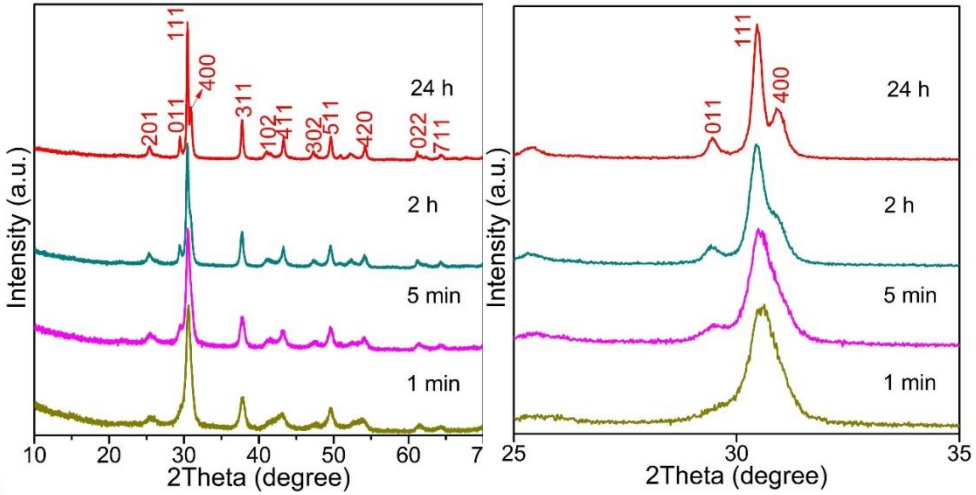


n-Type SnSe Nanoparticles

Adv. Energy Mater., 2017, **7**, 1602328

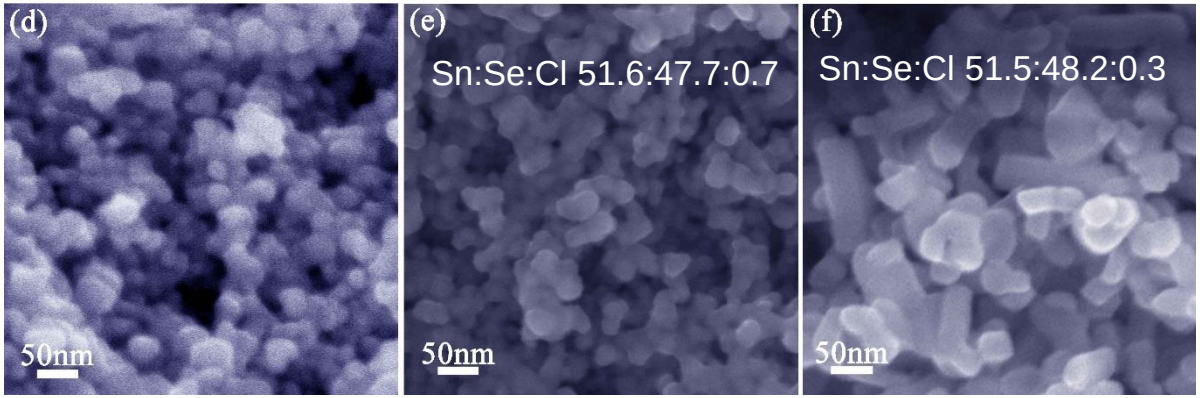
Carrier doping in nano-tin chalcogenides





Increasing particle size

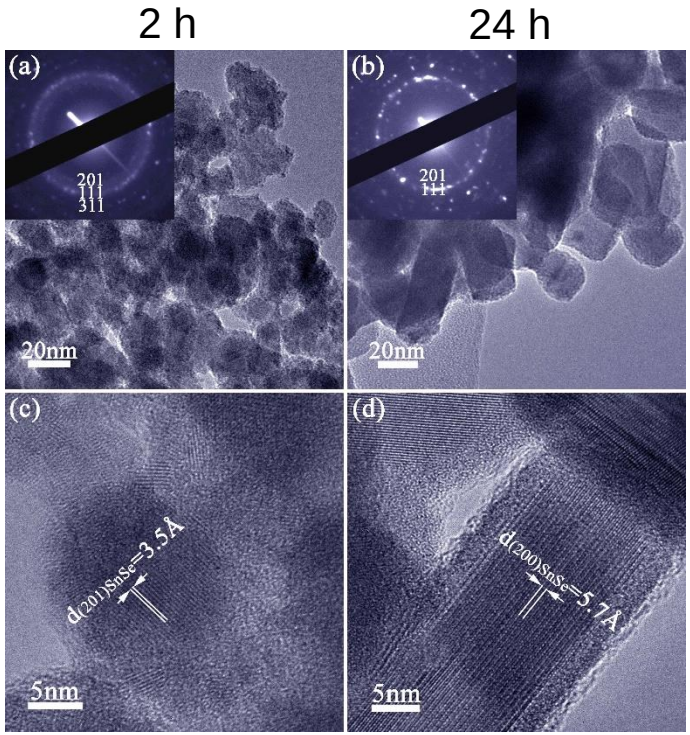
Increasing Cl content

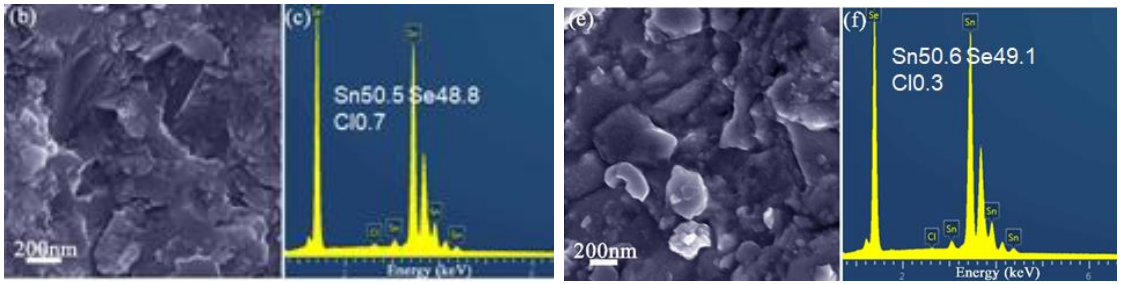


1 min 5 min 24 h

Adv. Energy Mater., 2017, **7**, 1602328

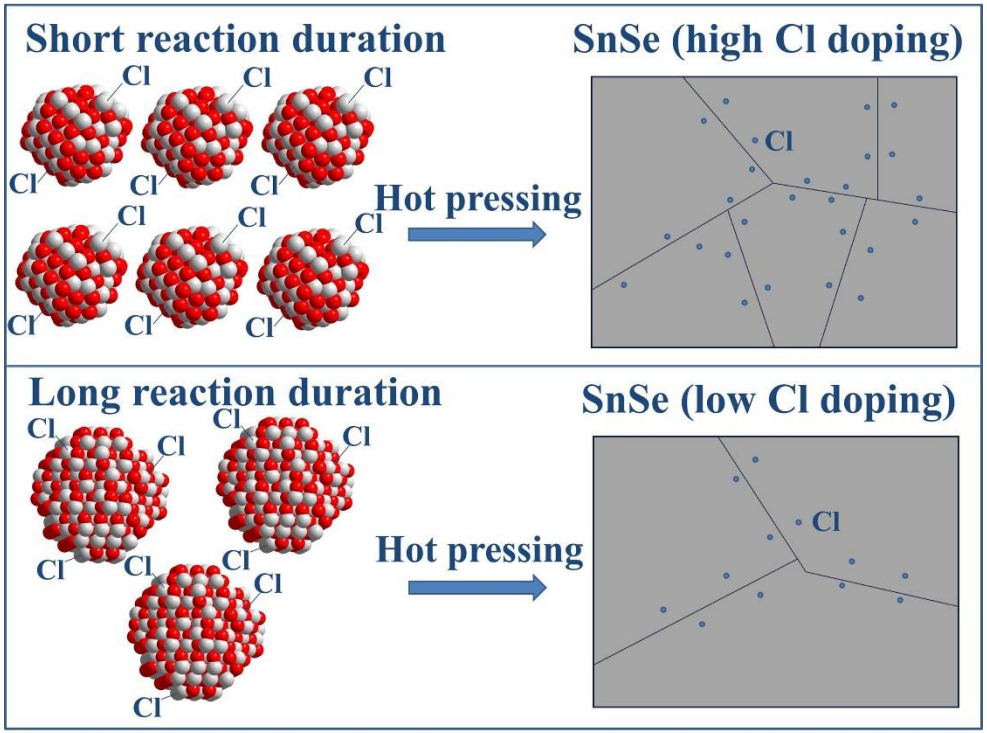
Carrier doping in nano-tin chalcogenides





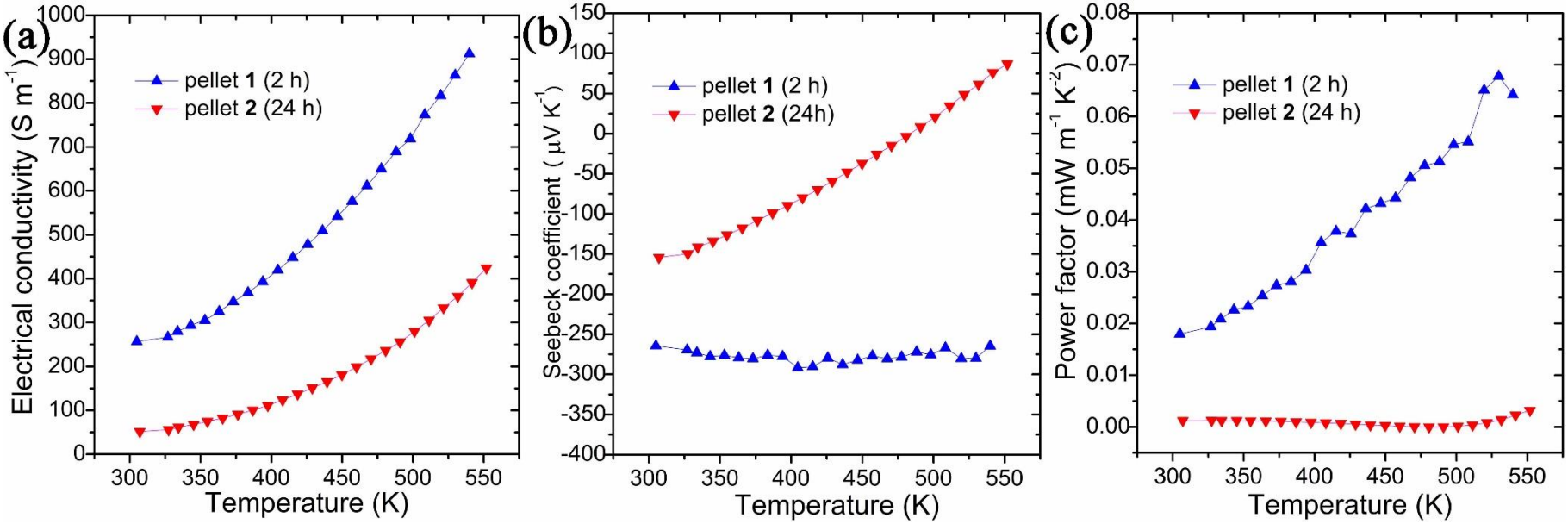
Pellet: 2 h

Pellet: 24 h



Adv. Energy Mater., 2017, **7**, 1602328

Carrier doping in nano-tin chalcogenides



React^{n} time	At% Cl	S_{300K} / μV K^{-1}	$\sigma_{300\ K}$ / S m^{-1}	n_H / 10^{18} cm^{-3}	μ_H / cm^2 V^{-1} s^{-1}
5 min	0.7	-295	185	3.47	2.66
2 h	0.6	-265	255	6.43	3.47
24 h	0.3	-145	55	2.56	0.85

Adv. Energy Mater., 2017, **7**, 1602328

University of Glasgow

Chemical Design of Chalcogenide Thermoelectrics

1. Introduction
   - The challenges
   - Heat to power; thermoelectrics
   - The state of the art

2. Chemically-designed chalcogenide thermoelectrics
   - Nanostructuring tin selenide, SnSe
   - Modifying chalcogenide composition – SnTe and SnS
   - Carrier doping in nano-tin chalcogenides

3. Summary

University of Glasgow

Summary

- Properties of tin chalcogenides can be modified via composition, doping and nanostructuring.
- Simple, quick, and energy-efficient solution syntheses yield SnSe, SnTe and SnS nanostructures in gram quantities.
- Topotactic anion exchange allows engineering of solid solutions of nanometric $SnS_{1-x}Se_x$.
- Tuneable semiconductivity (p-, n-type) via halide doping.
- Exceptional thermoelectric power factors surpass those of polycrystalline and surfactant-coated counterparts.

Acknowledgements

Group:

Dr Guang Han,

Co-workers and collaborators:

Dr J-W Bos, Dr S, Popuri; Heriot-Watt

Prof W Zhou, Dr H Greer; St Andrews

Prof M Reece, Dr R Zhang; QMUL

Prof D Paul, Dr L Ferre-Llin; Glasgow

Prof A. Knox (Glasgow) and the SUNTRAP team

Funding:

EPSRC,

The University of Glasgow,

WestCHEM.