Anharmonic effects in thermoelectric and 2D materials

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General outline

1. Thermoelectric monochalcogenides (part 1)
   - Bulk SnSe and SnS
   - Monolayer SnSe

2. 2D materials (part 2)
   - Graphene

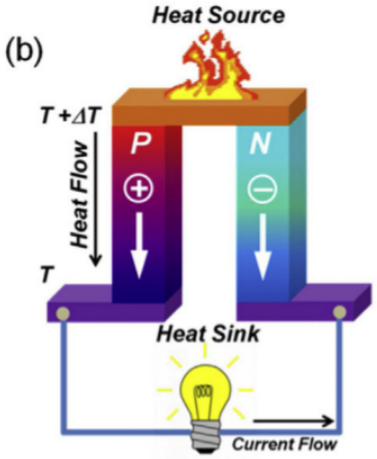
Outline

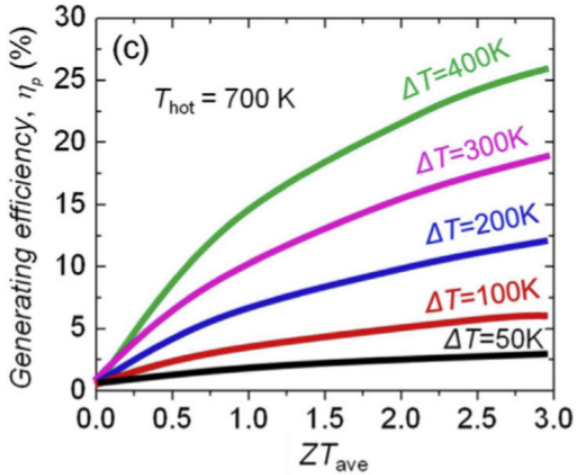
- Introduction
- Theoretical framework
- Part 1: Thermoelectric monochalcogenides
- Part 2: 2D materials
- Conclusions

Introduction

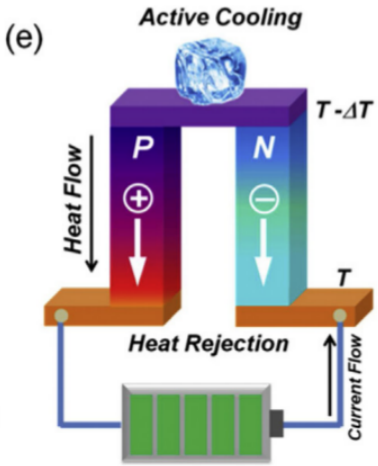
$$ZT = \frac{S^2 \sigma T}{\kappa}, \qquad S = -\frac{\Delta V}{\Delta T}$$

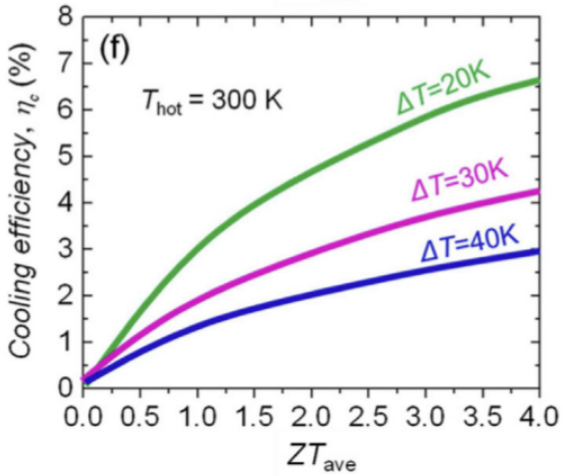
Thomas Johann Seebeck
German (1770-1831)





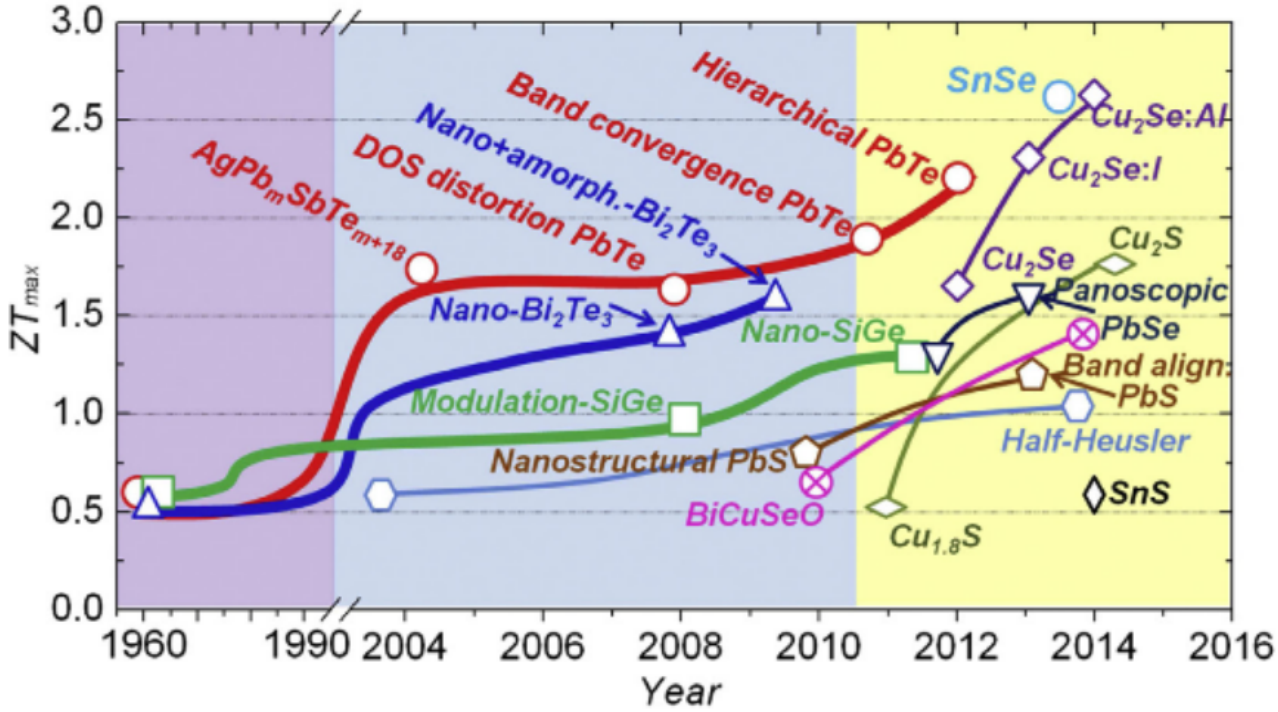
Jean Charles Athanase Peltier
French (1785-1845)





X. Zhang, L-D. Zhao / Journal of Materiomics 1 (2015) 92-105

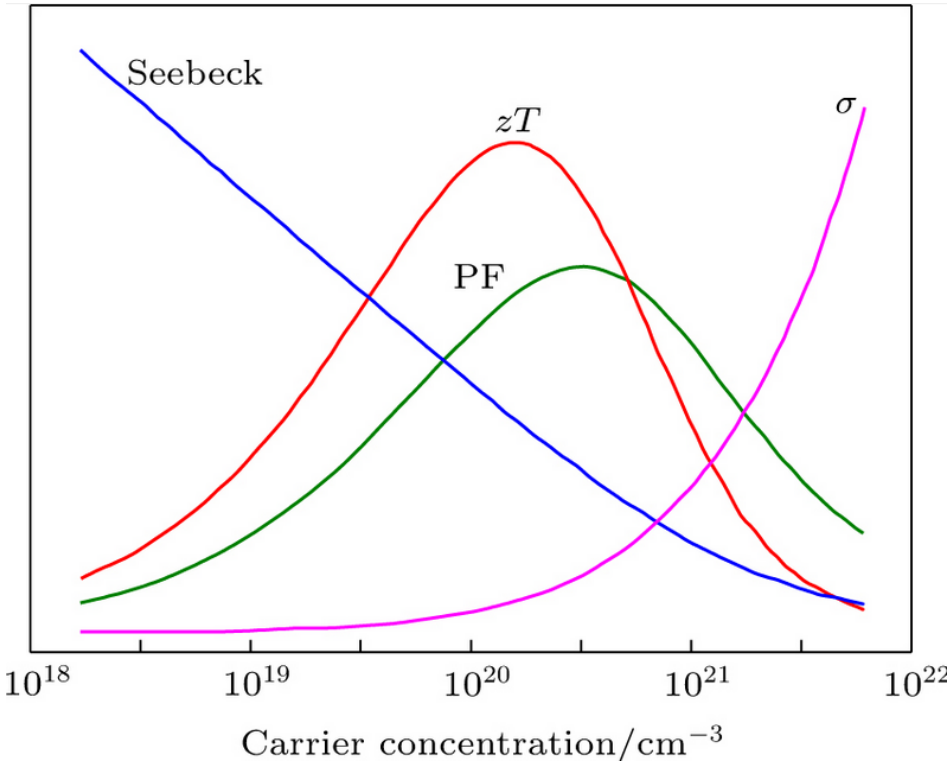
Introduction



- ZT_{max} low and in narrow temperature ranges
- Very limited technological applications.

X. Zhang, L-D. Zhao / Journal of Materiomics 1 (2015) 92-105

Introduction



- The physical magnitudes that define ZT are correlated
- How to overcome:
  - Doping + nanostructuring
  - Proximity to phase transitions
  - ...

Introduction

LETTER

doi:10.1038/nature13184

Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals

Li-Dong Zhao[1], Shih-Han Lo[2], Yongsheng Zhang[2], Hui Sun[3], Gangjian Tan[1], Ctirad Uher[3], C. Wolverton[2], Vinayak P. Dravid[2] & Mercouri G. Kanatzidis[1]

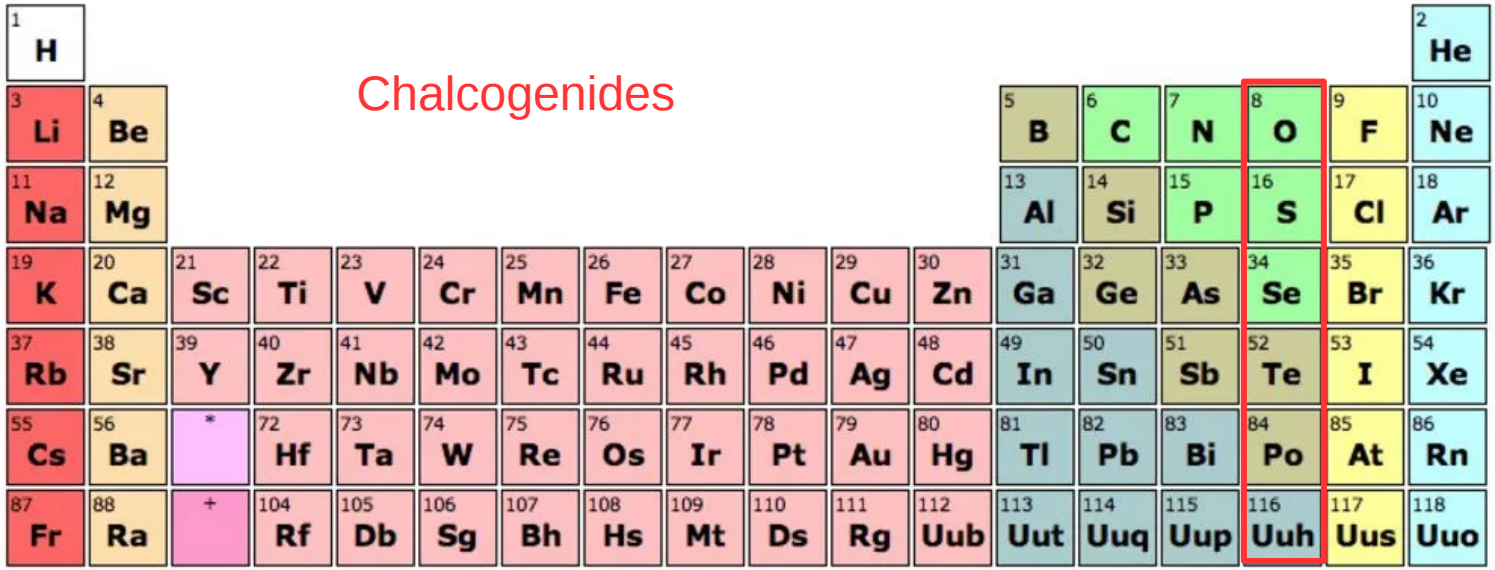
The thermoelectric effect enables direct and reversible conversion between thermal and electrical energy, and provides a viable route for power generation from waste heat. The efficiency of thermoelectric materials is dictated by the dimensionless figure of merit, *ZT* (where *Z* is the figure of merit and *T* is absolute temperature), which governs the Carnot efficiency for heat conversion. Enhancements above the generally high threshold value of 2.5 have important implications for commercial deployment[1,2], especially for compounds free of Pb and Te. Here we report an unprecedented *ZT* of 2.6 ± 0.3 at 923 K, realized in SnSe single crystals measured along the *b* axis of the room-temperature orthorhombic unit cell. This material also shows a high *ZT* of 2.3 ± 0.3 along the *c* axis but a significantly reduced *ZT* of 0.8 ± 0.2 along the *a* axis. We attribute the remarkably high *ZT* along the *b* axis to the intrinsically ultralow lattice thermal conductivity in SnSe. The layered structure of SnSe derives from a distorted rock-salt structure, and features anomalously high Grüneisen parameters, which reflect the anharmonic and anisotropic bonding. We attribute the exceptionally low lattice thermal conductivity (0.23 ± 0.03 W m^{-1} K^{-1} at 973 K) in SnSe to the anharmonicity. These findings highlight alternative strategies to nanostructuring for achieving high thermoelectric performance.

power factor (along the *b* axis), but, even more surprisingly, we observe that the thermal conductivity of SnSe is intrinsically ultralow (<0.25 W m^{-1} K^{-1} at >800 K), resulting in $ZT = 2.62$ at 923 K along the *b* axis and 2.3 along the *c* axis; these represent the highest *ZT* values reported so far for any thermoelectric system. Along the *a* direction, however, *ZT* is significantly lower, ~0.8. Here, it should be noted that SnSe along the *b* axis shows a room-temperature $ZT = 0.12$, which is comparable to the room-temperature value of 0.15 reported earlier[19]. SnSe, however, reveals high *ZT* values near and above the transition temperature of 750 K at which the structure converts from *Pnma* to *Cmcm*[20–22]. Such ultrahigh *ZT* along two principal directions and the observed crystallographic and *ZT* anisotropy prompted us to investigate the scientific underpinning of these intriguing results.

SnSe adopts a layered orthorhombic crystal structure at room temperature, which can be derived from a three-dimensional distortion of the NaCl structure. The perspective views of the room-temperature SnSe crystal structure along the *a*, *b* and *c* axial directions are shown in Fig. 1a–d. There are two-atom-thick SnSe slabs (along the *b*–*c* plane) with strong Sn–Se bonding within the plane of the slabs, which are then linked with weaker Sn–Se bonding along the *a* direction[20]. The structure contains highly distorted $SnSe_7$ coordination polyhedra, which have

- The best thermoelectric material so far: Intrinsic semiconductor with low lattice thermal conductivity ($\kappa = \kappa_{el} + \kappa_l$)

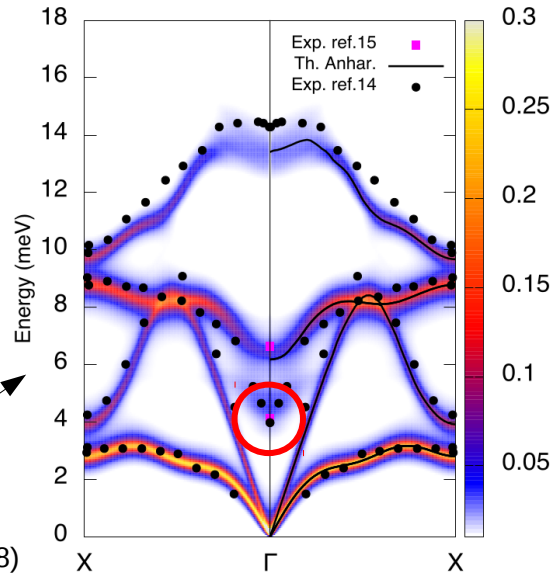
Introduction



Monochalcogenides: PbTe, SnTe, GeTe, SnS...

Low lattice thermal conductivity

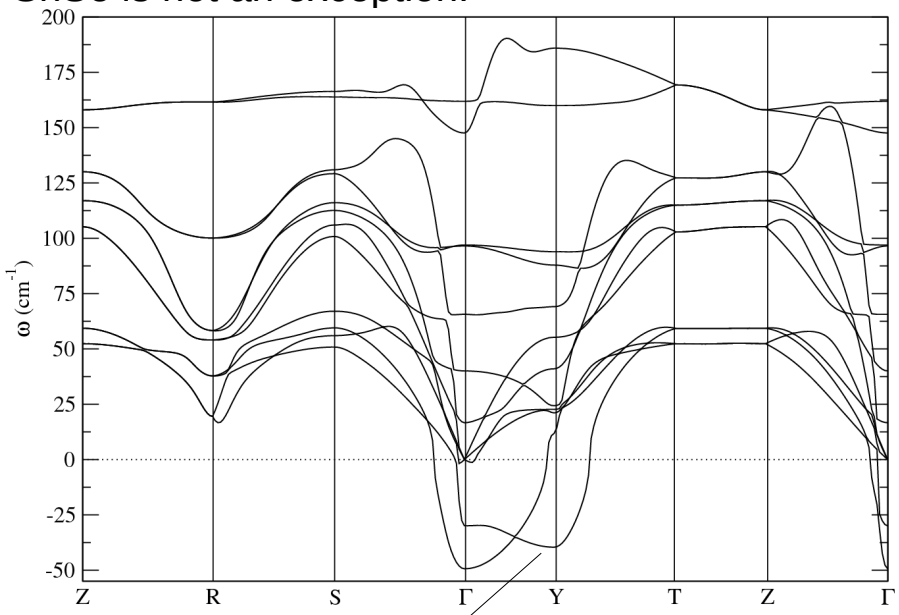
They show strongly anharmonic features:
- Lattice instabilities in the harmonic phonons
- Ferroelectric transitions
- Incipient ferroelectricity
- Special features in the phonon spectral function

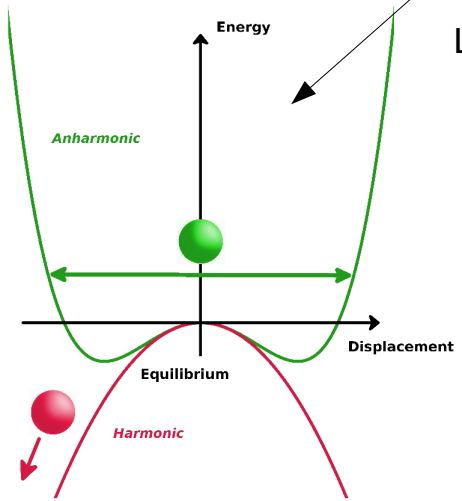


G. A. Ribeiro et al. Physical Review B 97, 014306 (2018)

Introduction

SnSe is not an exception:



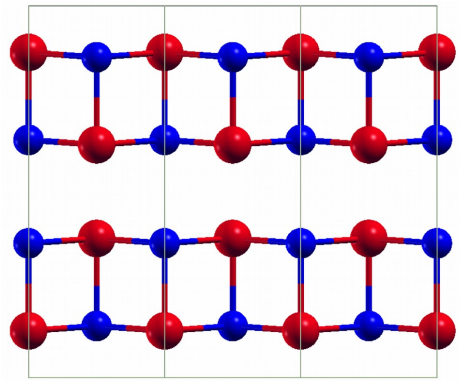


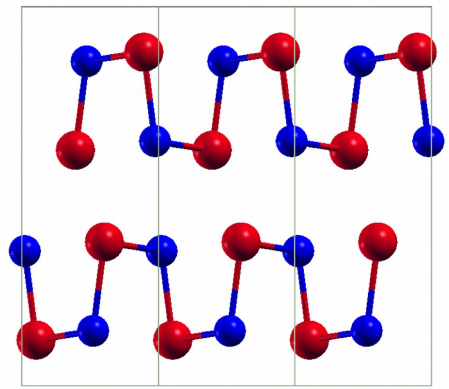
LATTICE INSTABILITIES

PHASE TRANSITION

Tc = 800 K

High T
Cmcm





Low T
Pnma

Very low lattice thermal conductivity 0.3-1.0 W/mK (800 K)