On Thermoelectric Properties of P-Type Skutterudites

Jihui Yang
Materials Science and Engineering Department
University of Washington

present at The 3rd TE Applications Workshop
Baltimore, MD
March 21, 2012

Contributors:
Jiong Yang (UW)
James R. Salvador, Gregory P. Meisner, Mike Reynolds, and Francis Stabler (GM)
Xun Shi, Shenqiang Bai, Wenqing Zhang, and Lidong Chen (SIC)
Hsin Wang and David Singh (ORNL)
John Copley and Jack Rush (NCNR)

Outline

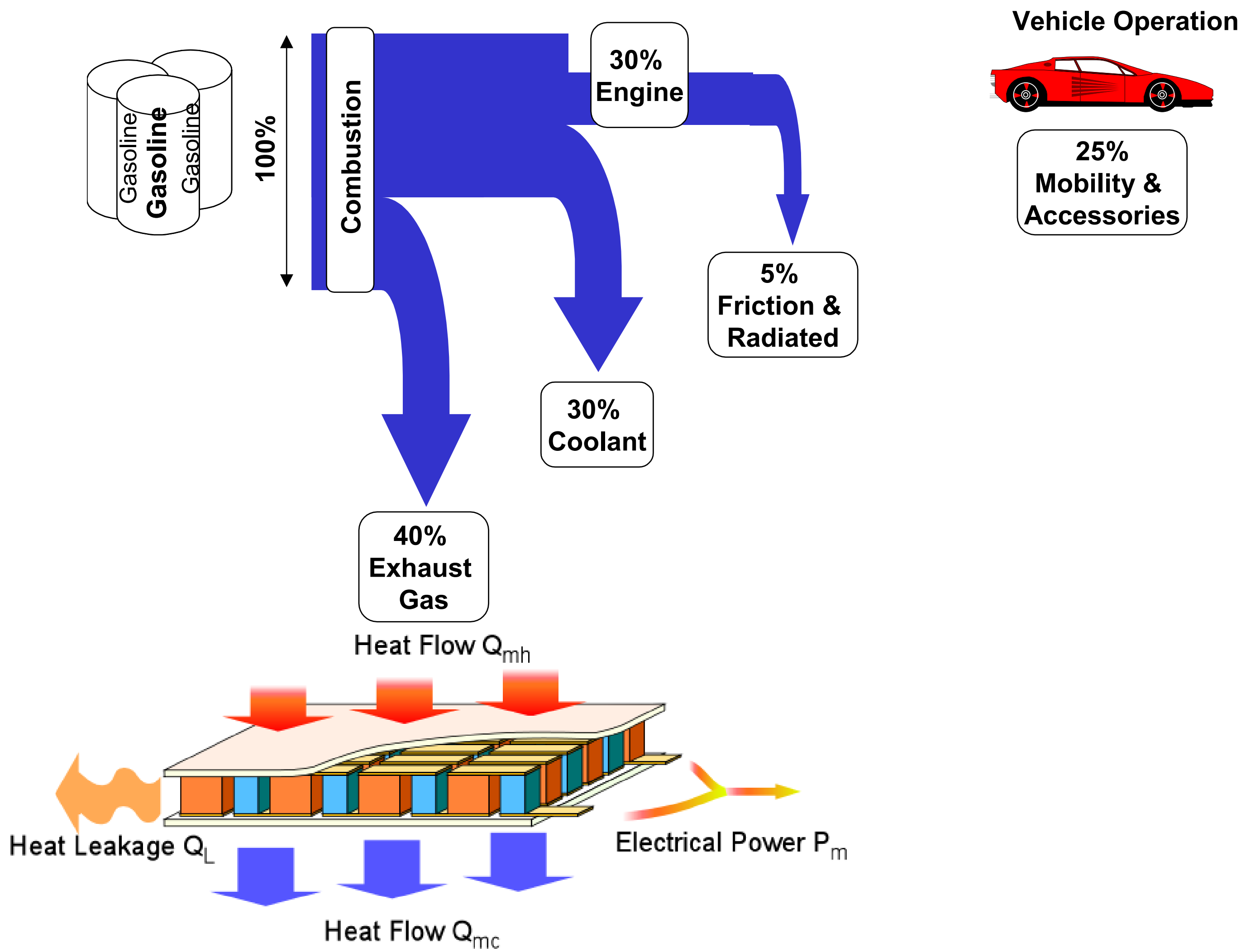
- Automotive Waste Heat Recovery

- N-type skutterudites (PRL 95, 185503, 2005; PRL 102, 175508, 2009; JACS 131, 5560, 2009; JACS. 133, 7837, 2011)
  - Multiple Frequency Resonant Phonon Scattering
  - κ_{min} at elevated temperatures
  - $ZT_{max} \cong 1.7$

- P-type Skutterudites
  - Lattice thermal Conductivity – filler phonon mode coherence, bipolar effect
  - Carrier transport – electron-phonon interaction
  - 5*d* transition metal based p-type

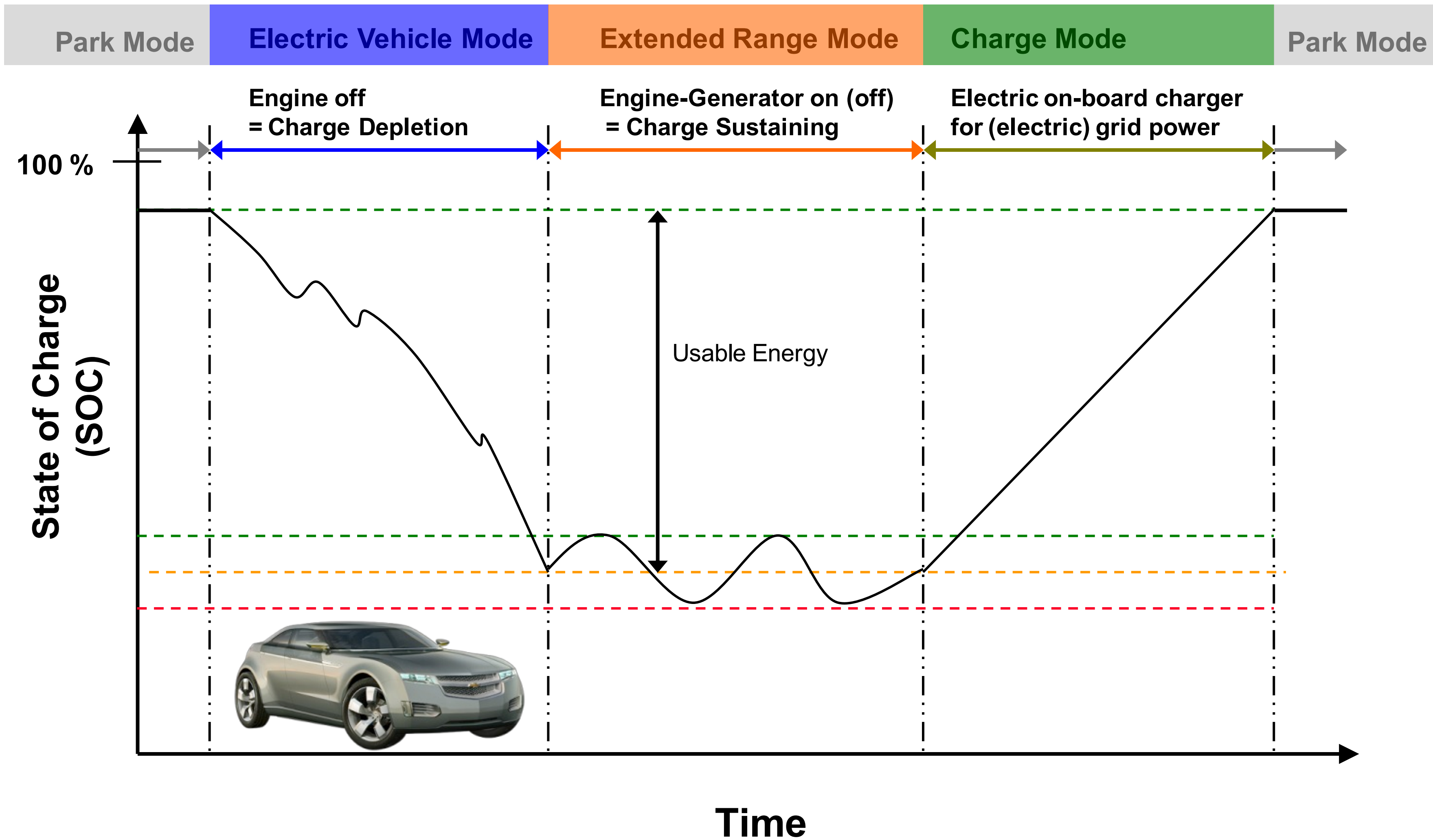
- Conclusion

Typical Energy Path in Gasoline Fueled Internal Combustion Engine Vehicles

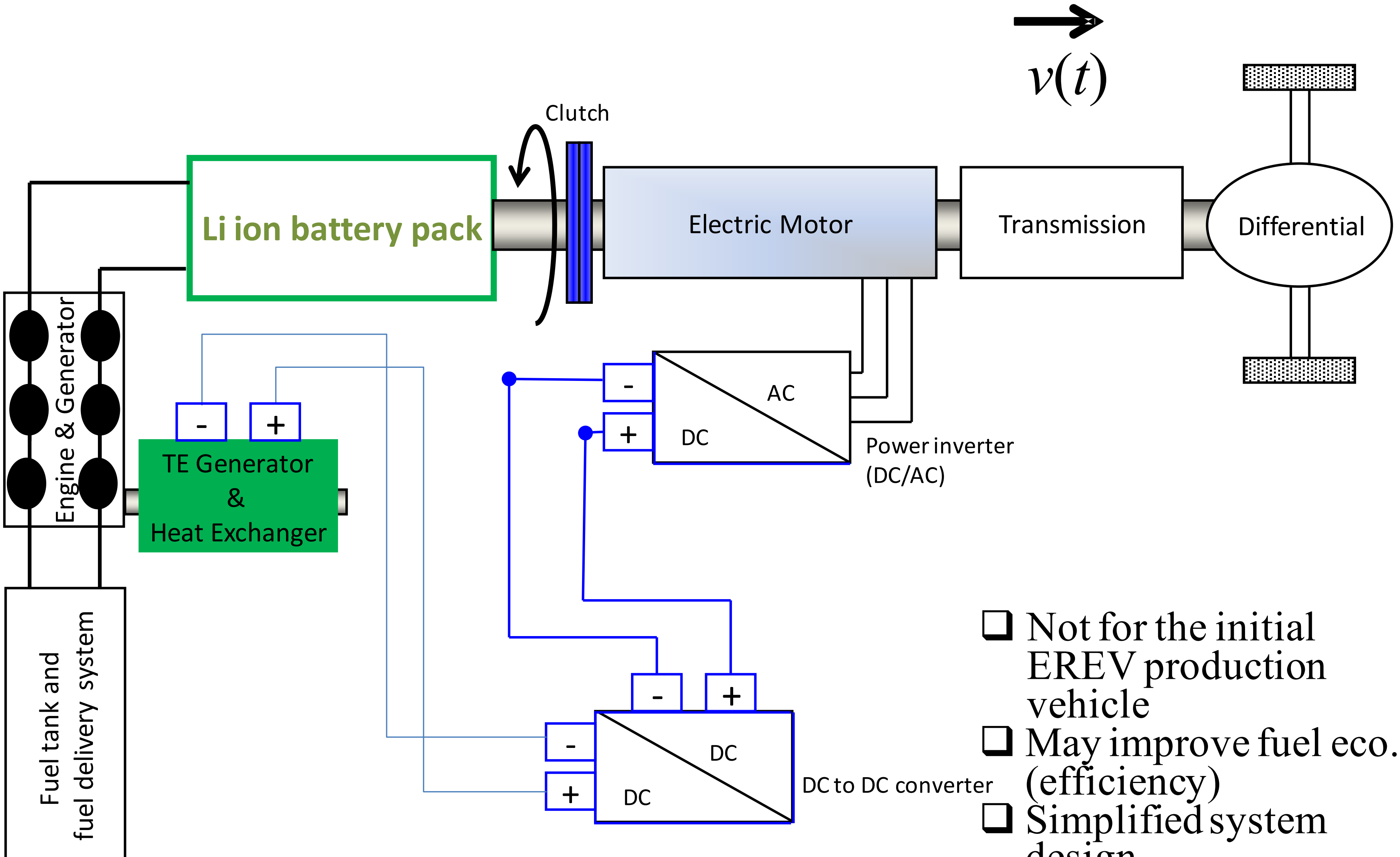


- ❑ Today's ICE-based vehicles: < 20% of fuel energy is used for propulsion
- ❑ > 60% of gasoline energy (waste heat) is not utilized

E-REV Operation Modes



Compelling Concept: Thermoelectric Augmented E-REV



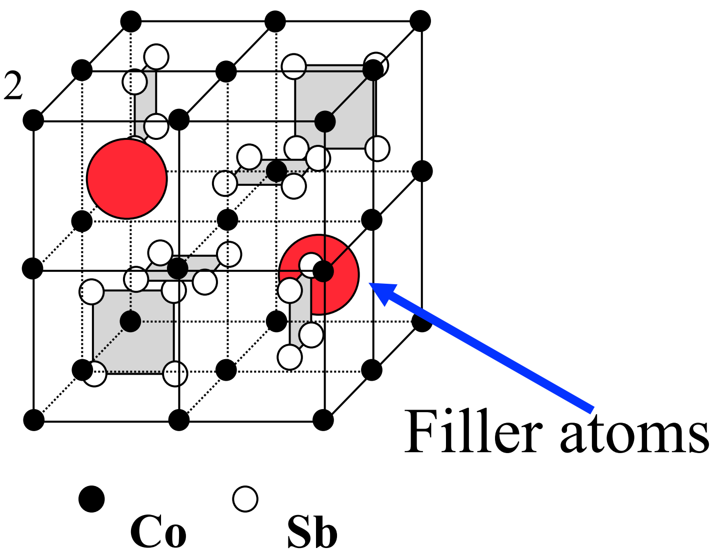
- ❑ Not for the initial EREV production vehicle
- ❑ May improve fuel eco. (efficiency)
- ❑ Simplified system design

Skutterudites 101

- $CoAs_3$ -based minerals found in region of Skutterud, Norway
- Compounds with the same crystal structure are known as "skutterudites"

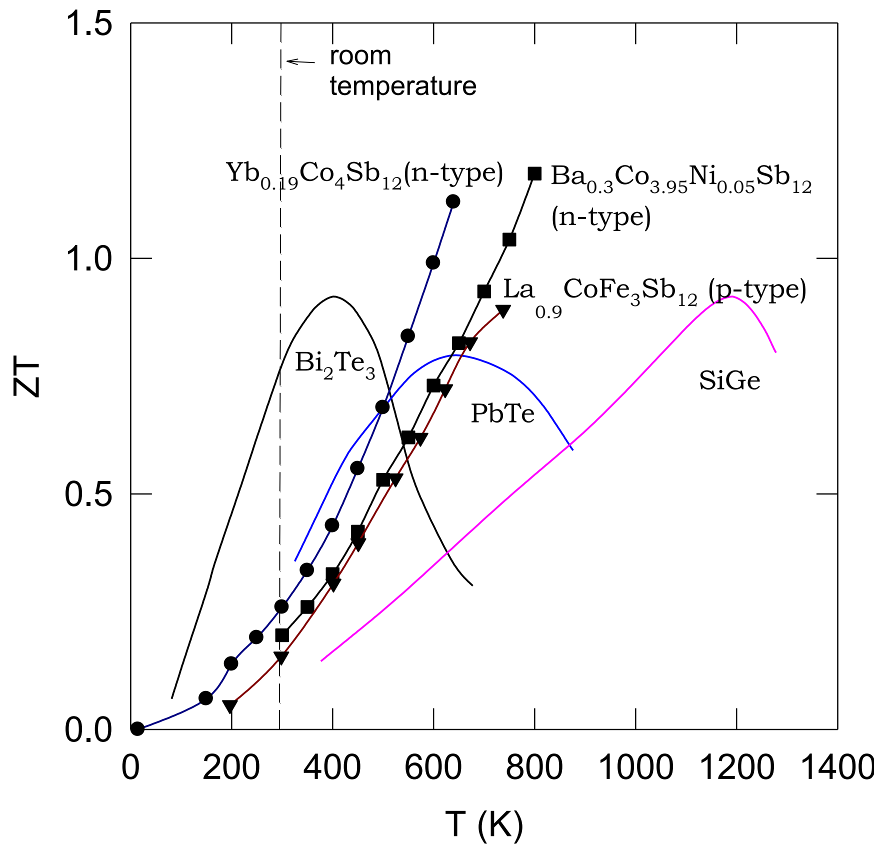
Skuterud gård, Modum

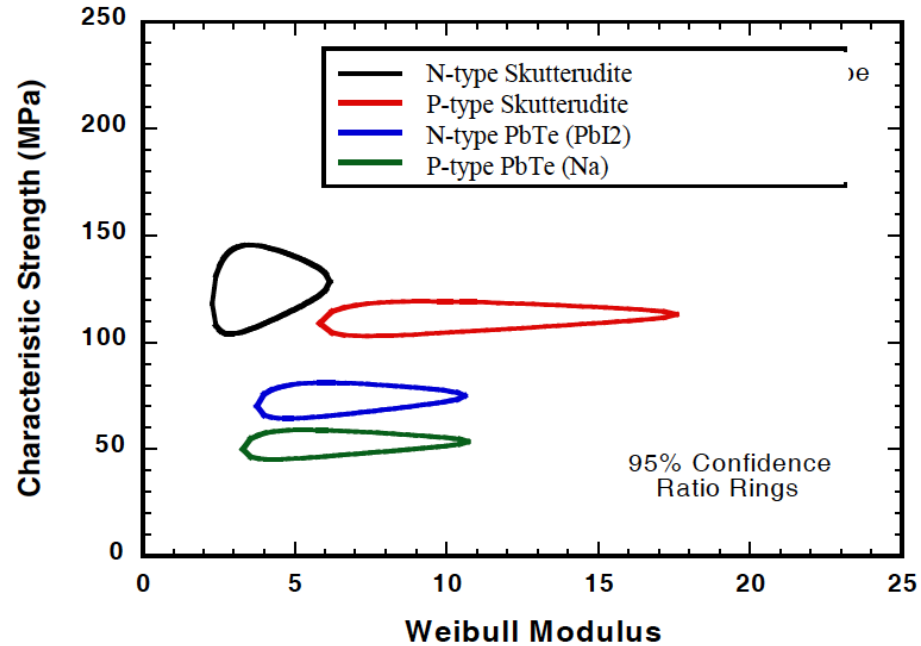
□Co_4Sb_{12}



1. Slack, et al., JAP **76**, 1665 (1994)
2. Morelli, et al., JAP **77**, 3777 (1995)

Excellent Thermoelectric & Thermomechanical Property

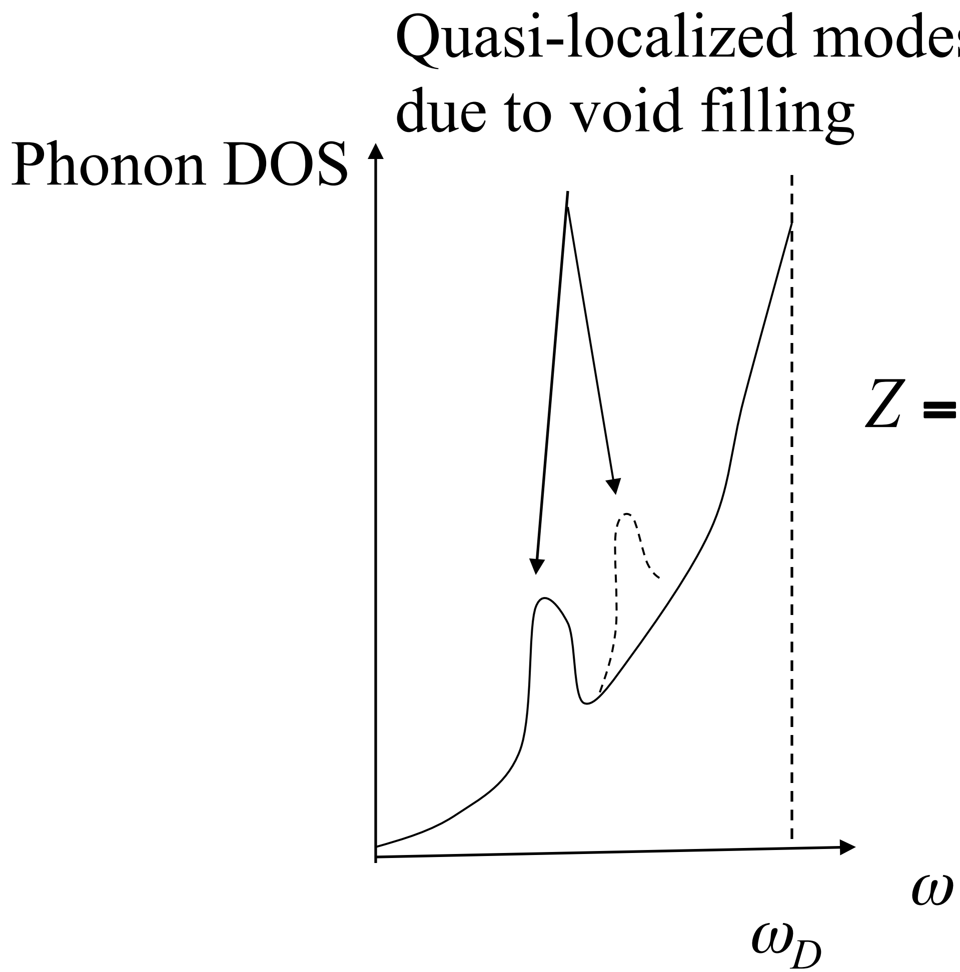




1. Nolas et al., APL 77, 1855 (2000)
2. Dyck et al., JAP 91, 3698 (2002)
3. Sales, et al., Science 272, 1325 (1996)
4. Salvador et al., Philo. Mag. 89, 1517 (2009)

- ❑ **Prospective TE power generation materials for automotive waste heat recovery**
- ❑ **Both the n- and p-type exist – optimal for TE module construction**
- ❑ **The materials are mechanically strong**

Hypothesis - Double-filled Skutterudites for Additional κ_L Reduction?



$$Z = \frac{S^2}{\kappa_T \rho} = \frac{S^2}{(\kappa_L + \kappa_e)\rho}$$

- ❑ localized modes at frequencies sufficiently different from one another would scatter a broader range of heat carrying lattice phonons, hence, achieving even lower κ_L.

Phonon Resonant Frequencies

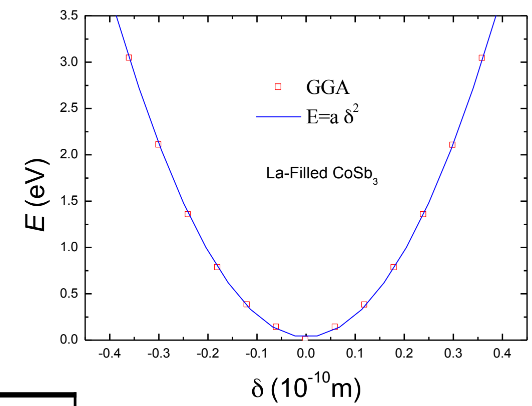
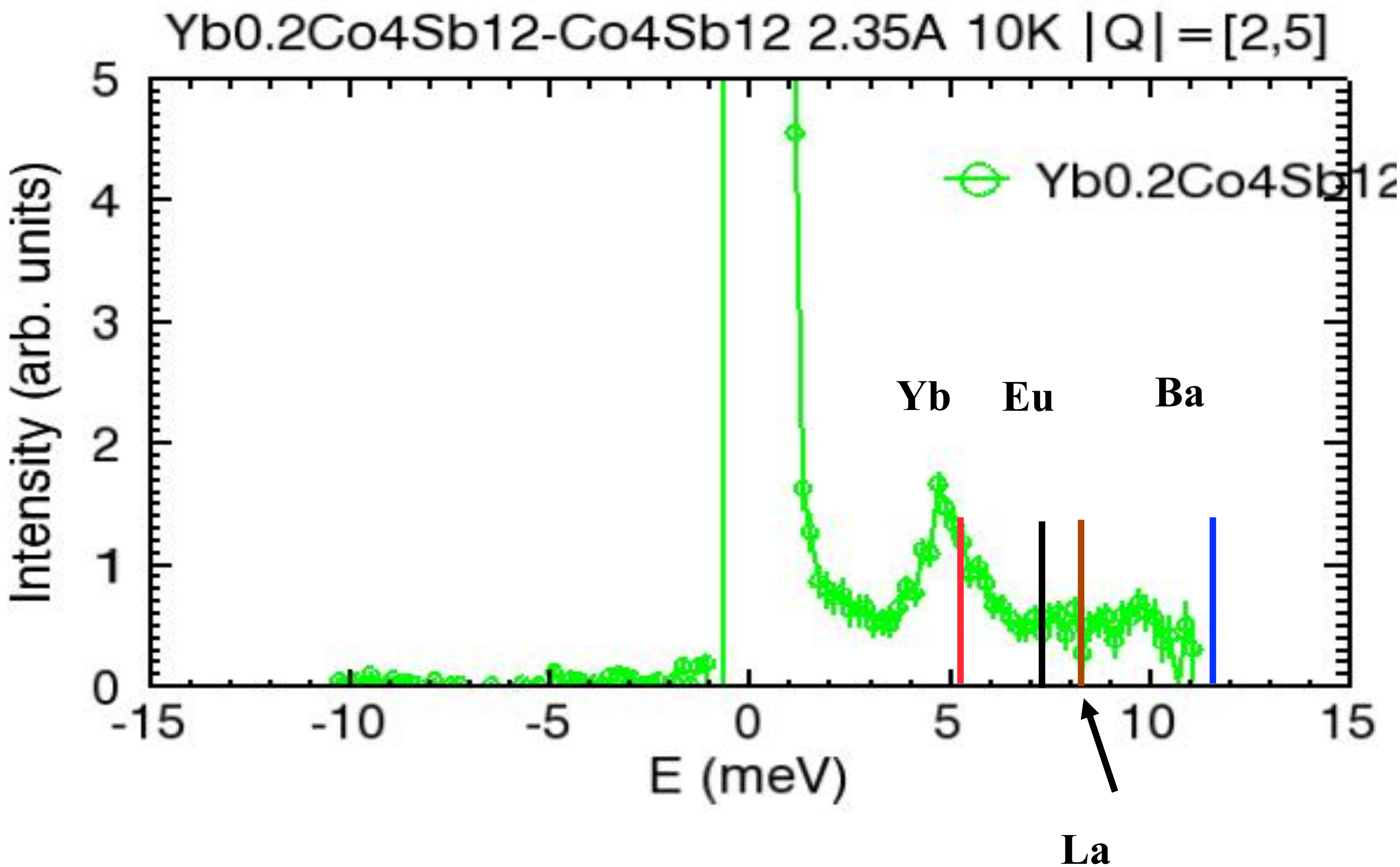


TABLE II. Spring constant k and resonance frequency ω_0 in the [111] and [100] directions of $R_{0.125}Co_4Sb_{12}$, where R = la, Ce, Eu, Yb, Ba, Sr, Na, and K.

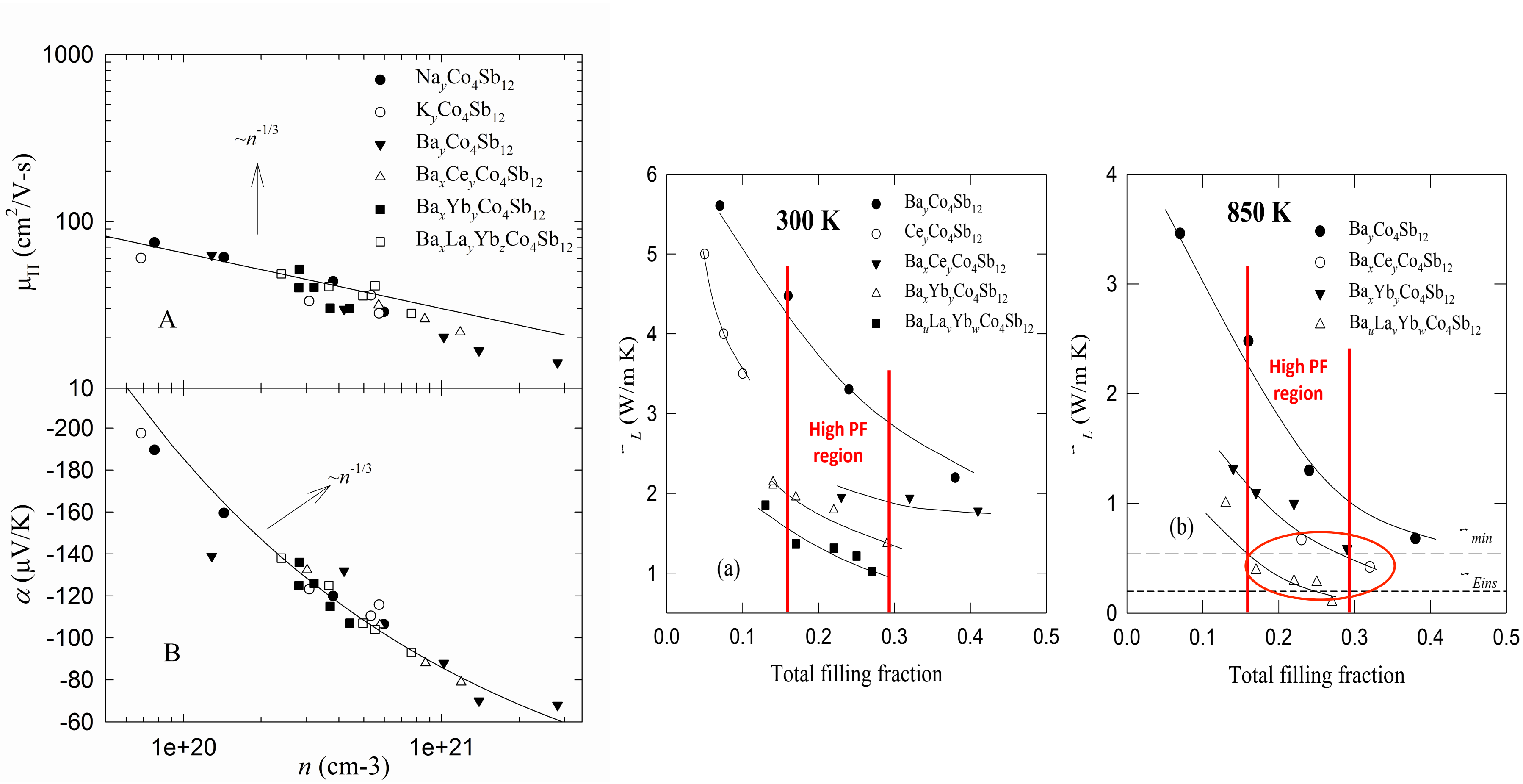
		[111]		*[100]*	
R	Mass (10^{-26} Kg)	k (N/m)	ω_0 (cm^{-1})	k (N/m)	ω_0 (cm^{-1})
La	23.07	36.10	66	37.42	68
Ce	23.27	23.72	54	25.18	55
Eu	25.34	30.16	58	31.37	59
Yb	28.74	18.04	42	18.88	43
Ba	22.81	69.60	93	70.85	94
Sr	14.55	41.62	90	42.56	91
Na	3.819	16.87	112	17.18	113
K	6.495	46.04	141	46.70	142

1. J. Yang, W. Zhang, S. Q. Bai, Z. Mei, and L. Chen, Appl. Phys. Lett. **90**, 192111 (2007)

Phonon DOS Measurement – Inelastic Neutron Scattering

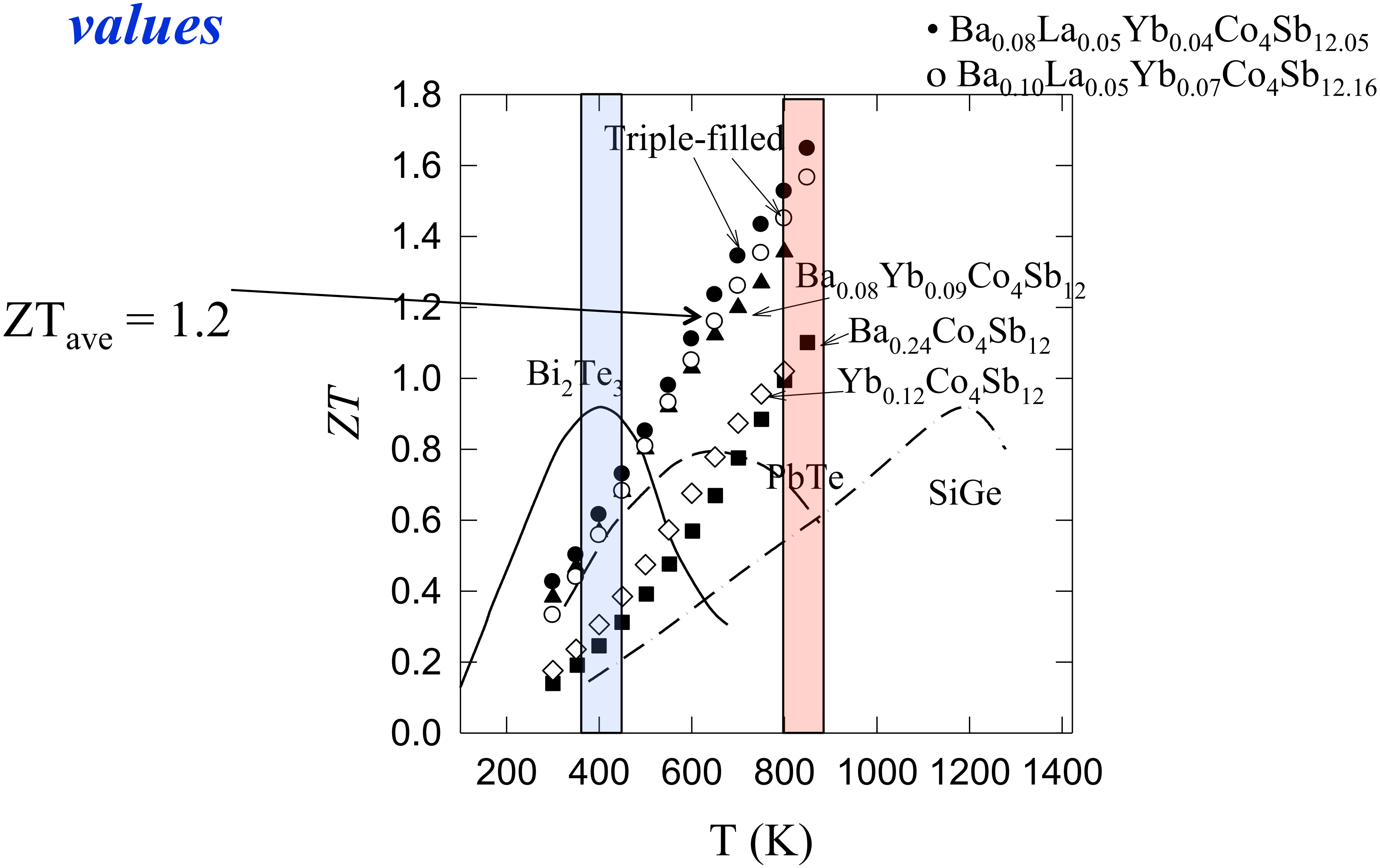


Lattice Thermal Conductivity Reduction without Power Factor Deterioration



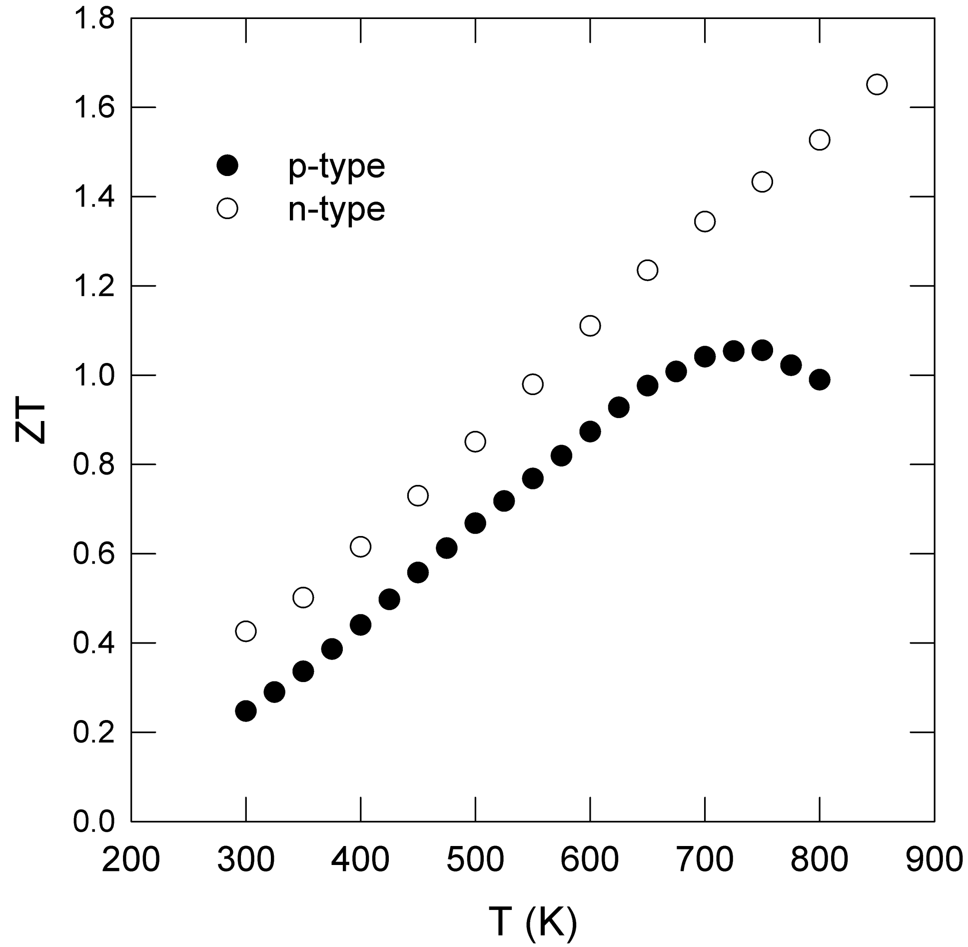
1. X. Shi, et al, JACS **133**, 7837 (2011)

Multiple-filled Skutterudites – Much Improved ZT values



1. X. Shi, et al. Appl. Phys. Lett. **92**, 182101 (2008)
2. X. Shi, et al, JACS **133**, 7837 (2011)

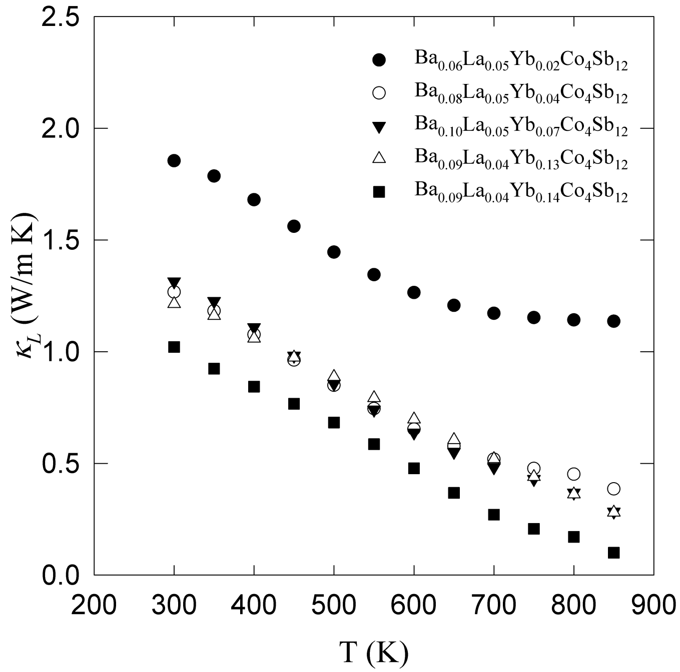
ZT Mismatch – Device Challenge



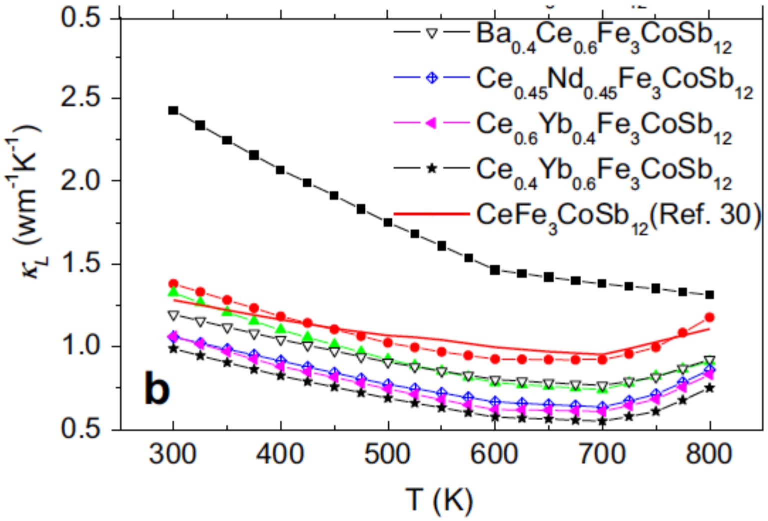
1. X. Shi, et al, JACS **133**, 7837 (2011)
2. R. Liu, et al., Intermetallics **19**, 1747 (2011)

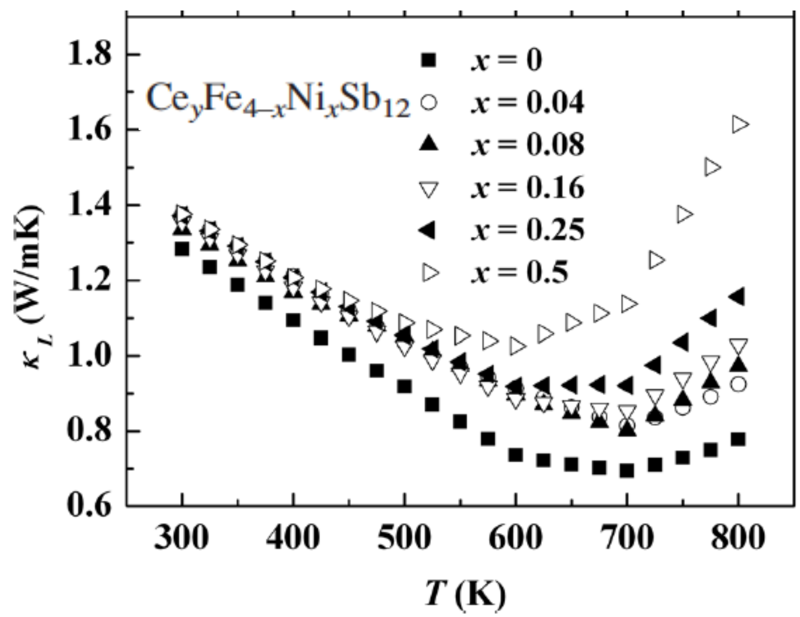
Lattice Thermal Conductivity

n-type



p-type

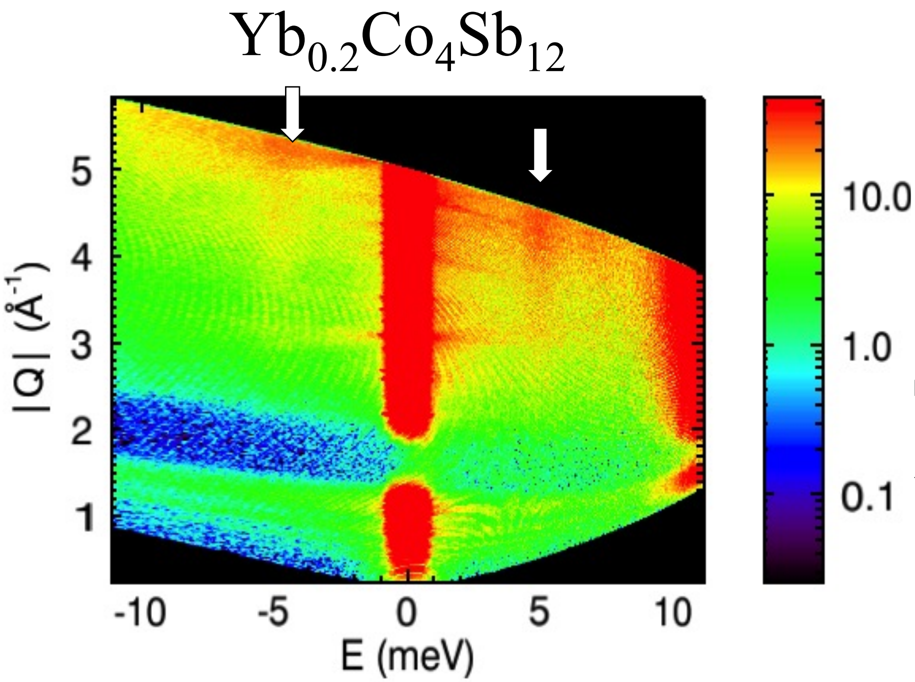


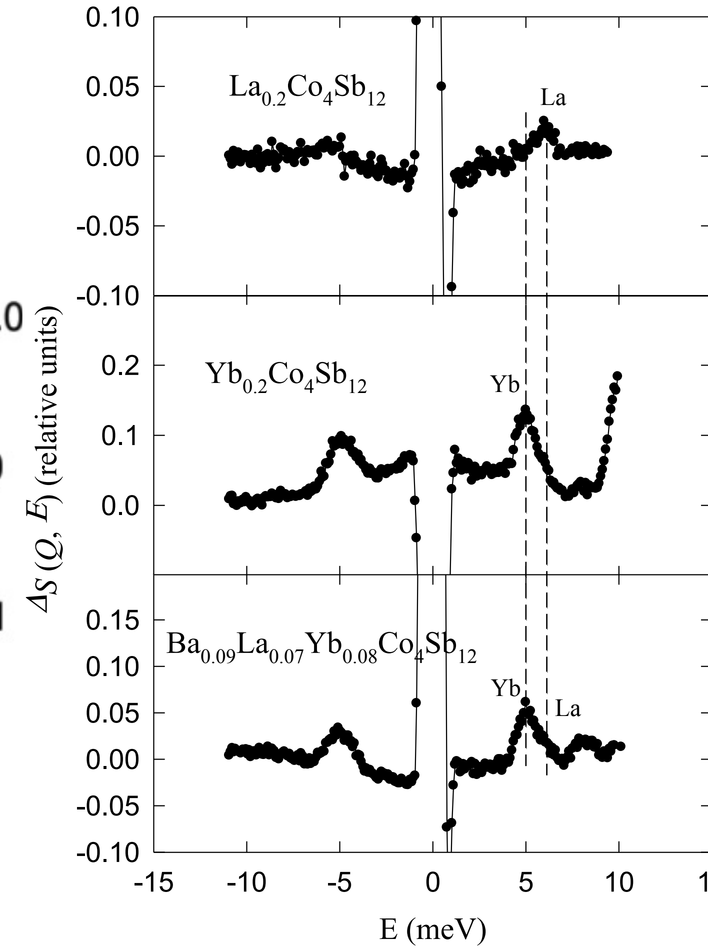


1. X. Shi, et al, JACS **133**, 7837 (2011)
2. R. Liu, et al., Intermetallics **19**, 1747 (2011)
3. Qiu et al., JAP **111**, 023705 (2012)
4. Cho et al., Acta Mater. 60, 2104 (2012)

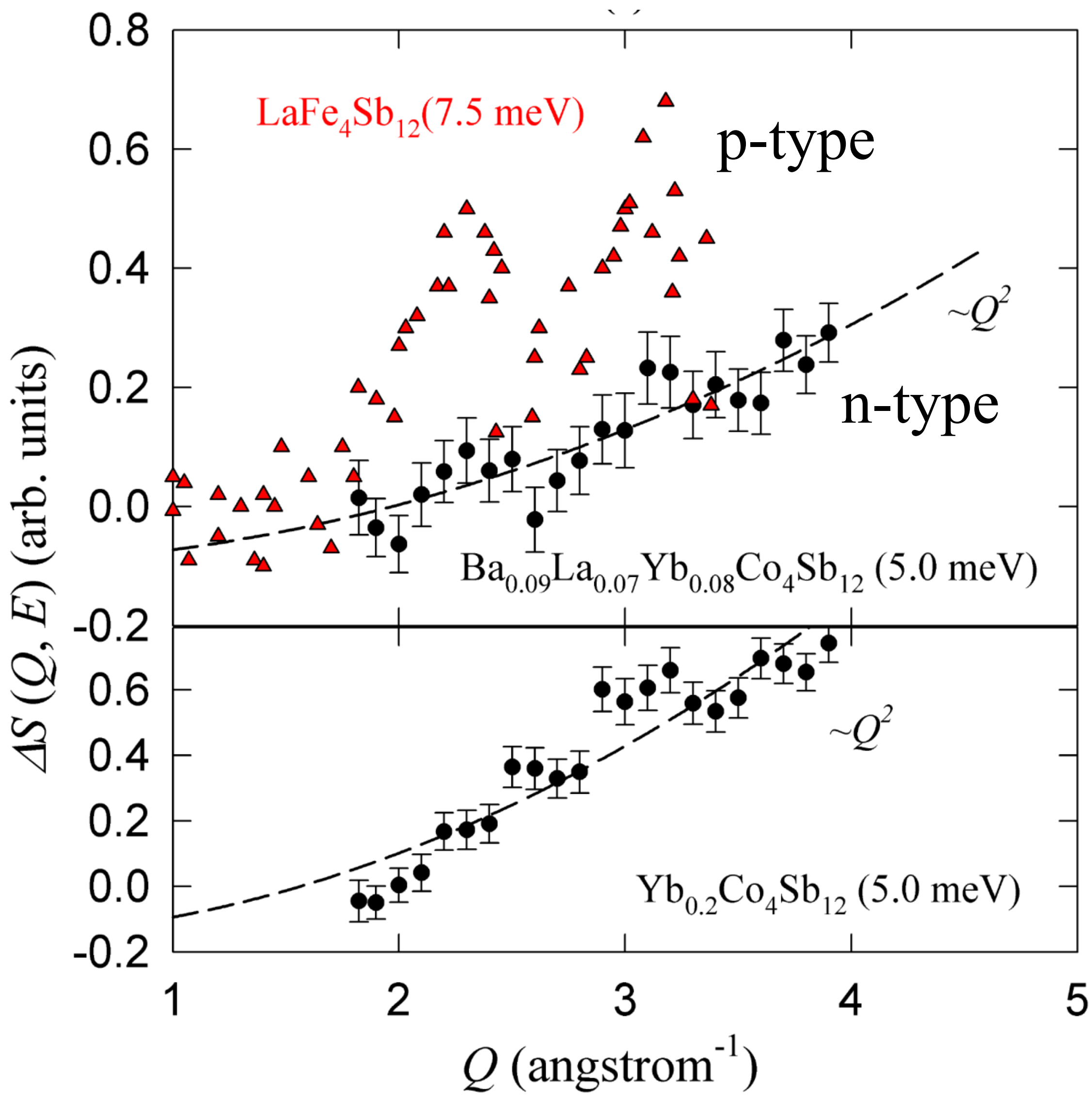
- ❑ p-type has higher κ_L, especially at high temperatures (bipolar effect)

Phonon DOS Measurement – Inelastic Neutron Scattering





Coherent vs. Incoherent



1. Koza et al., Nature Mater. 7, 805 (2008)
2. Shi et al., unpublished

- ❑ The incoherent rattler modes in the n-type result in lower κ_L

Bipolar Effect

$$\kappa_e = \kappa_n + \kappa_p + \frac{b}{(1+b)^2}\left(\frac{E_g}{k_B T} + 4\right)^2 \left(\frac{kB}{e}\right)^2 \sigma T$$

$$b = \mu_n / \mu_p$$

- Significant when the mobilities of the two charge carriers are similar
- This has been observed in Bi_2Te_3 and Si/Ge
- Electronic band structures need to be altered to mitigate the bipolar effect

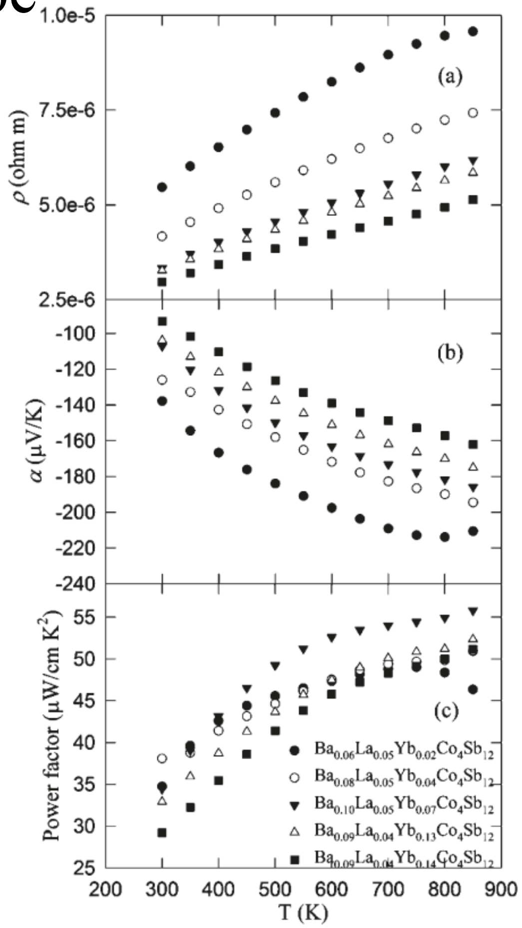
Glassbrenner et al., Phys. Rev. 134, A1058 (1964)

H.J. Goldsmid, Proc. Phys. Soc. B **69**, 203 (1956)

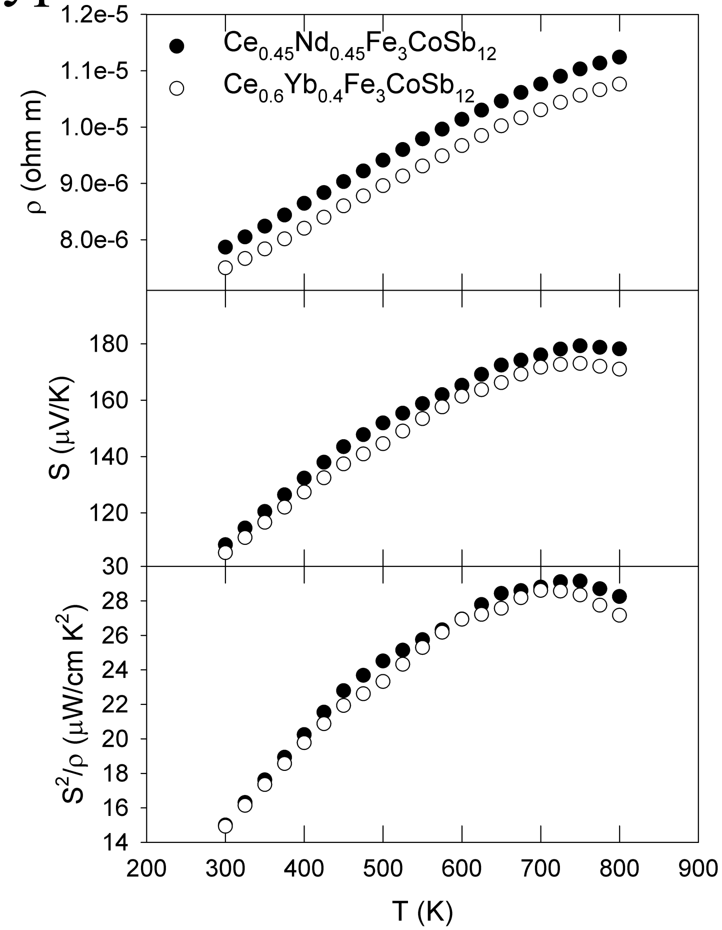
[55] J. R. Drabble and H. J. Goldsmid, *Thermal Conduction in Semiconductors* (Pergamon Press, Inc., London, 1961), pp. 104–119.

Electrical Transport Comparison

n-type $\leq 1\times10^{21}$ cm^{-3}



p-type $2\text{-}3\times10^{21}$ cm^{-3}



1. X. Shi, et al, JACS **133**, 7837 (2011)
2. R. Liu, et al., Intermetallics **19**, 1747 (2011)

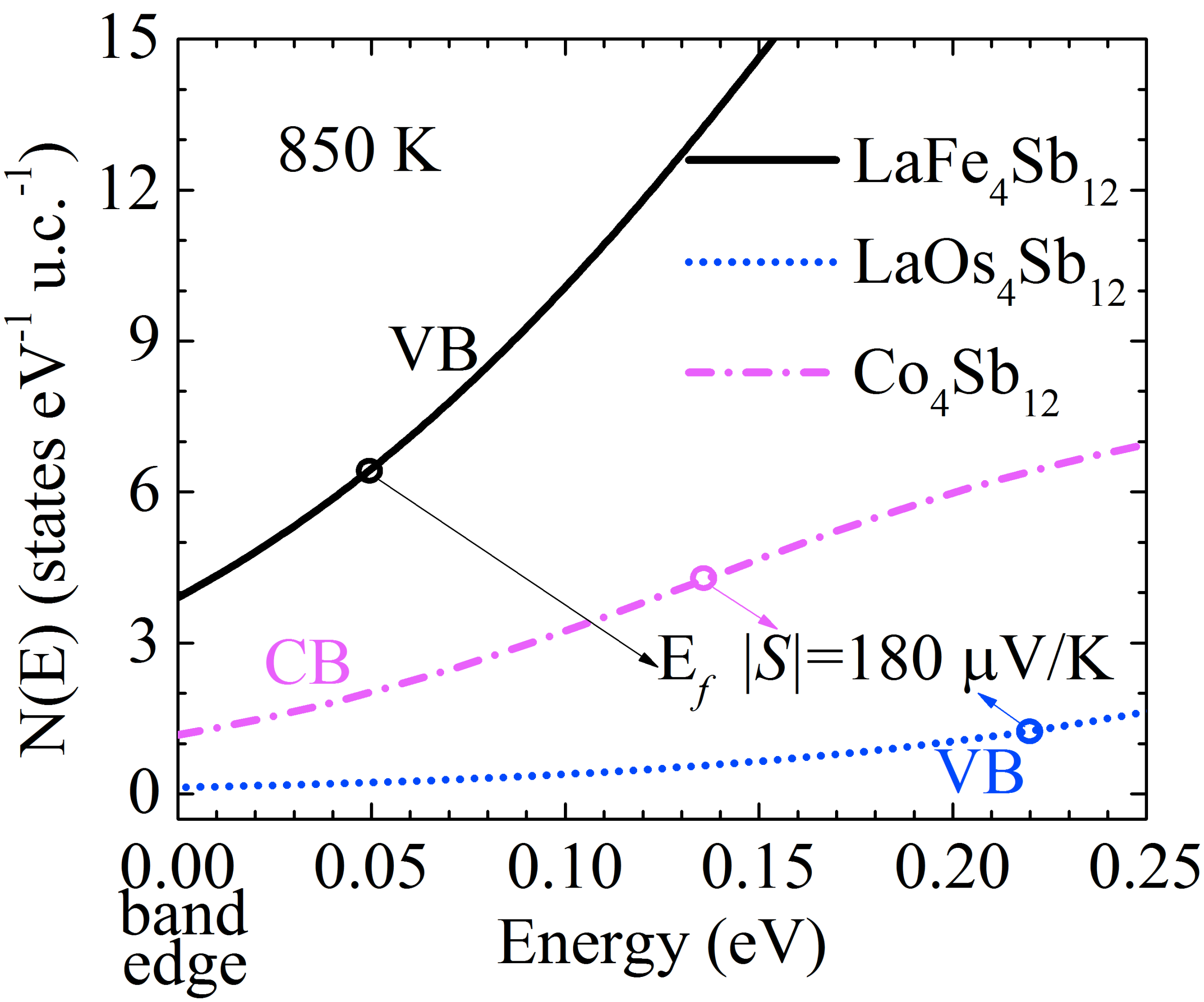
- The electrical resistivity of the p-type is about a factor of two too high

Electron-Phonon Interaction

$$\frac{1}{\tau} = \frac{\sqrt{2}\varepsilon_c^2 (m_p^*)^{3/2} k_B T}{\pi \hbar \rho c_l^2} E^{1/2} \propto N(E)$$

- For skutterudites, electron phonon interaction dominates charge carrier scattering at elevated temperatures
- The strength of e-ph interaction is proportional to the carrier density of states

5d Transition Metal-based P-Type Skutterudites

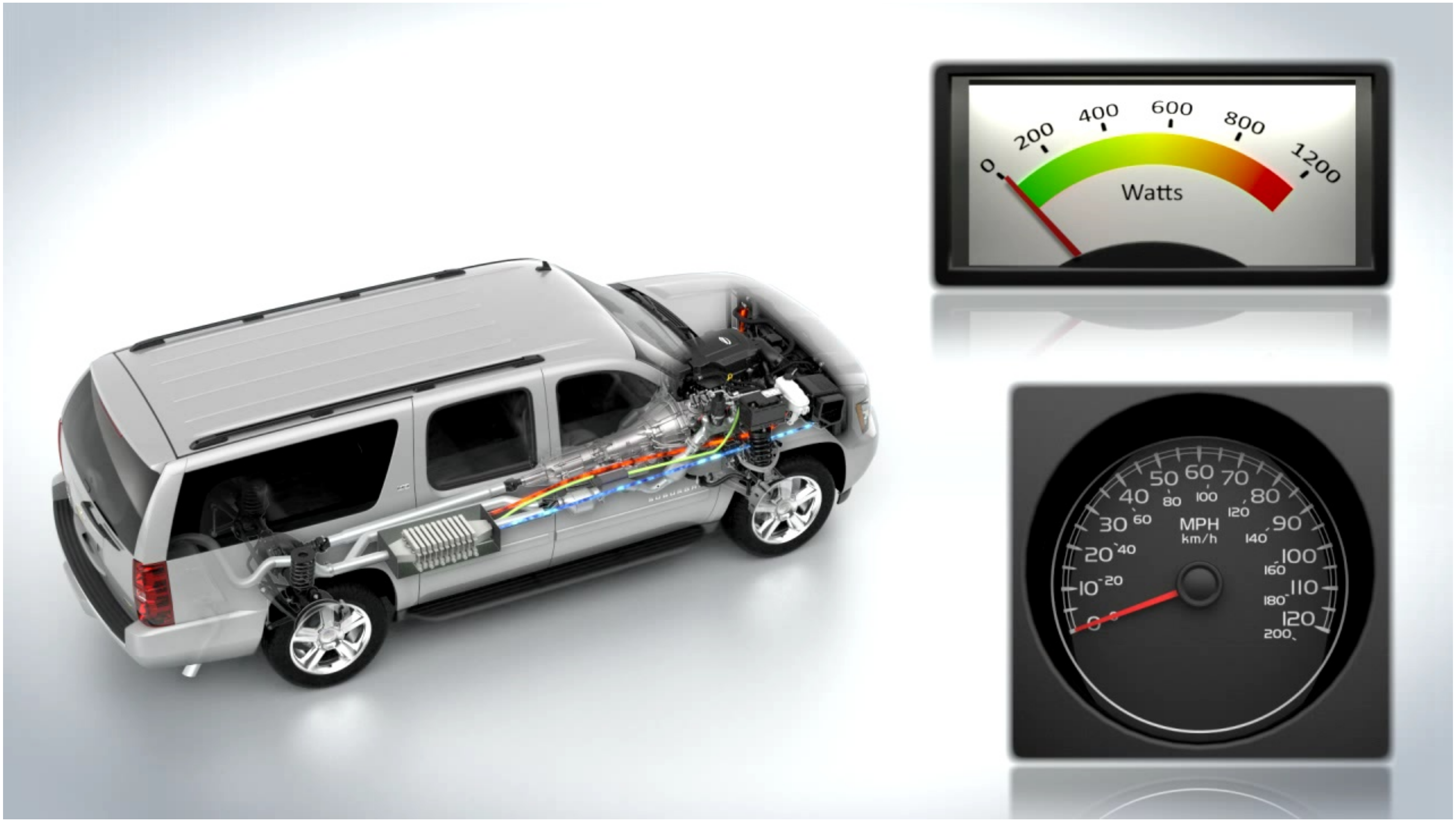


- ❑ 5*d* transition metal-based p-type skutterudites offers potential of reducing *ρ,* and hence power factor enhancement

Conclusions

- Skutterudites are leading material candidates for automotive exhaust waste heat recovery
- Multiple frequency resonant phonon scattering lead to very high ZT for the n-type
- High values of κ_L in the p-type arise from the coherent low energy phonon mode and the bipolar effect – ongoing topic
- Power factor in the p-type can be improved by 5-d transition metal substitution
- Current challenges with the p-type lie in their electron band structures

Thank You !


0
200
400
600
800
1200
Watts
10
20
30
40
50
60
70
80
90
100
110
120
MPH
km/h