Electrical and Thermal Transport Optimization of High Efficient n-type Skutterudites

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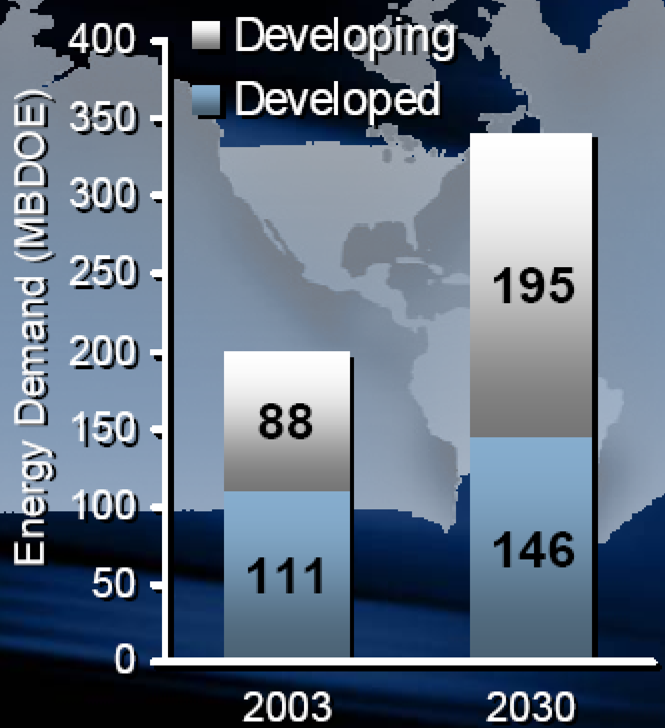
Outline

- ❑ Potential TE automotive applications
  - – The challenge
  - – Where does TE fit in the solution
  - – DOE program
- ❑ Multiple-filled skutterudites
  - – Structural and electrical transport
  - – Multiple filling on thermal conductivity
  - – High ZT and materials design principle
- ❑ Conclusions

The Challenge

- Global energy demand exceeds our current glide path for supply
- There are several risks that can disrupt the existing supply
  - Insufficient refinery capacity
  - Geopolitical issues
  - Natural disasters, wars and hostile regimes that take a significant amount of capacity offline
- Growing concern about Global Warming due to CO_2
- Potential for regulations that exceed both technical capability and business feasibility

Global increase 2% / year, 70% increase over 2003



Source: DOE Energy Information Agency

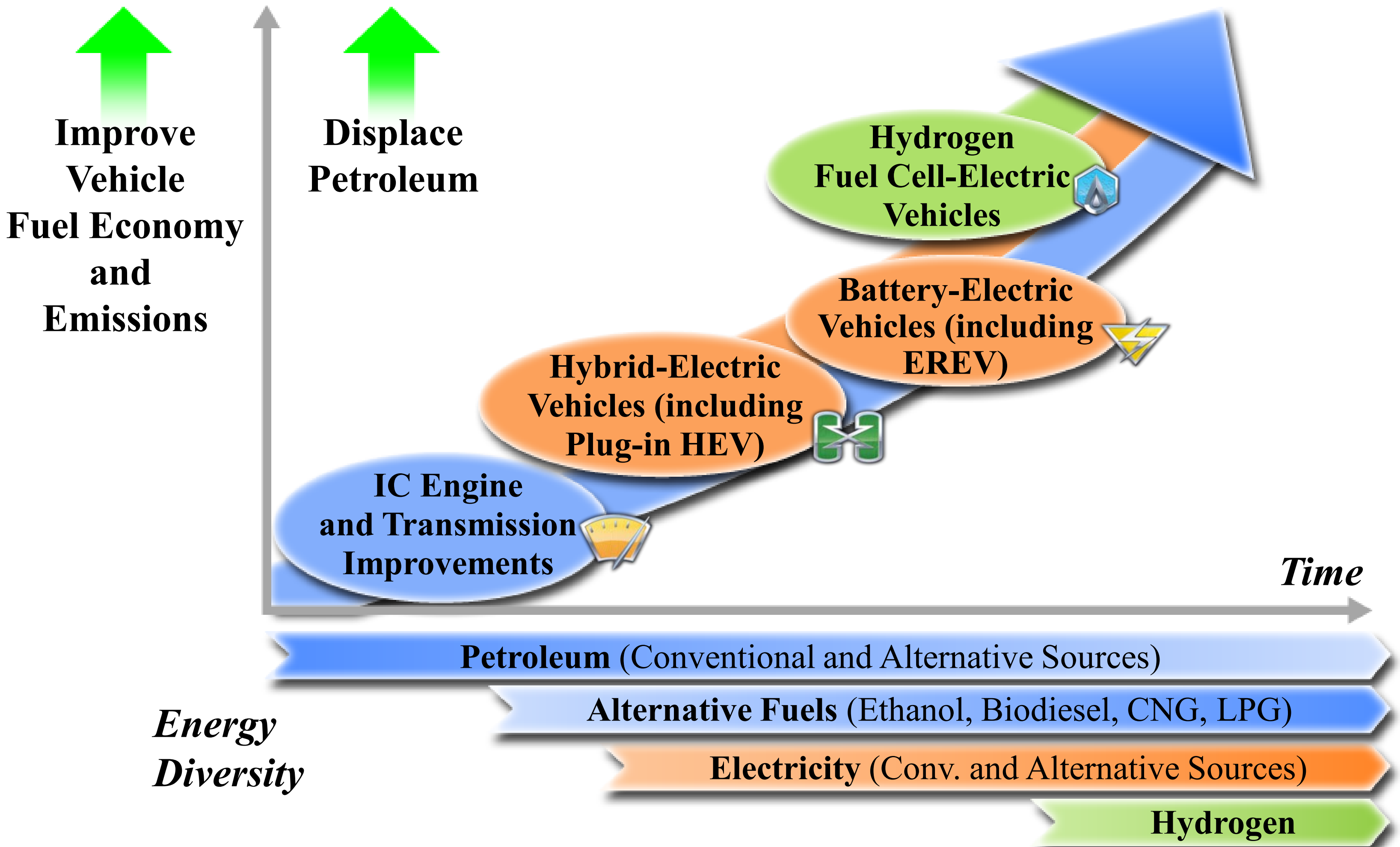
MBDOE: Millions of barrels per day oil equivalent

So What's the Solution?

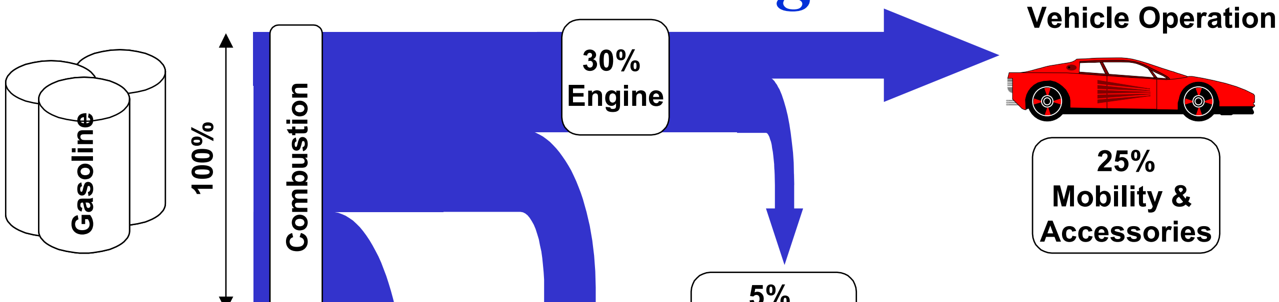
In GM's view we must

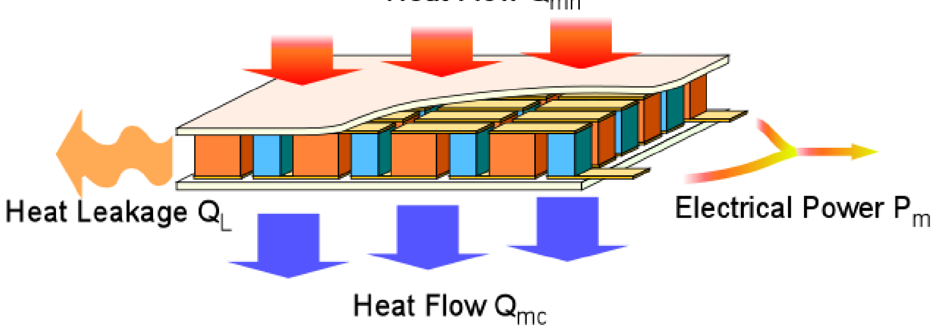
- ❑ Increase fuel efficiency of conventional propulsion vehicles in response to market demands
- ❑ Displace a portion of petroleum fuel usage
- ❑ Diversify energy sources for use in transportation applications
- ❑ Reduce net emissions of carbon dioxide

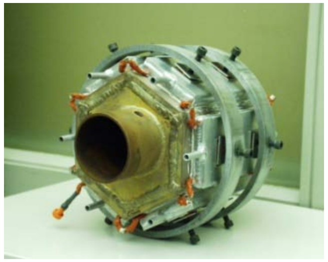
GM Advanced Propulsion Technology Strategy



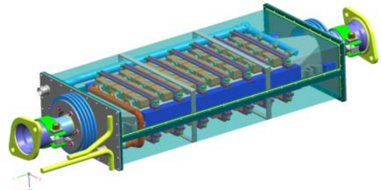
Typical Energy Path in Gasoline Fueled Internal Combustion Engine Vehicles





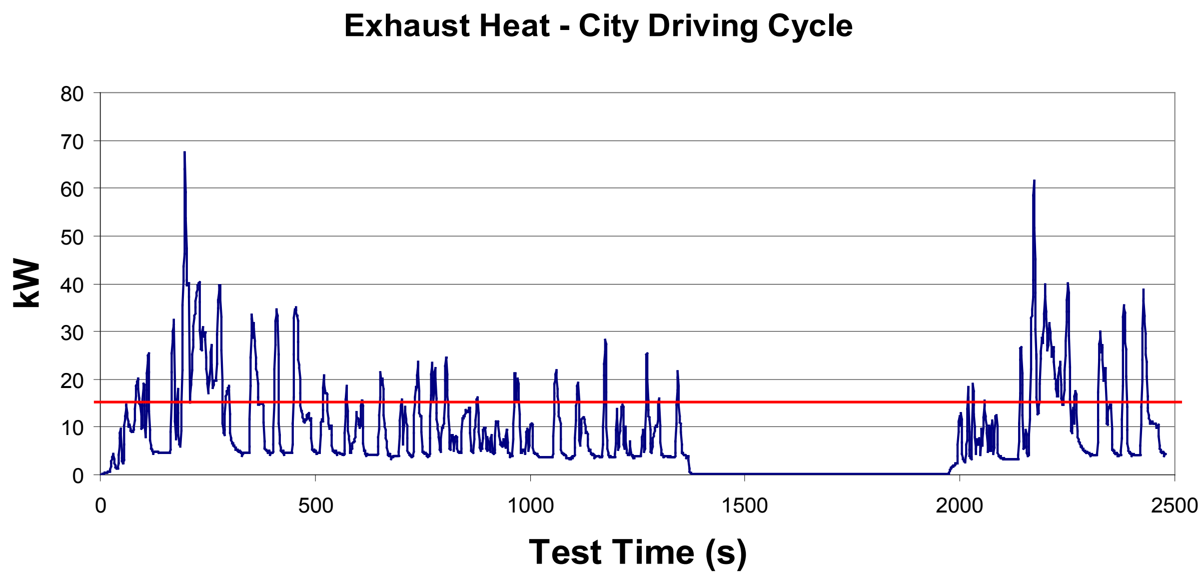

GEN I


GEN II


GEN III

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

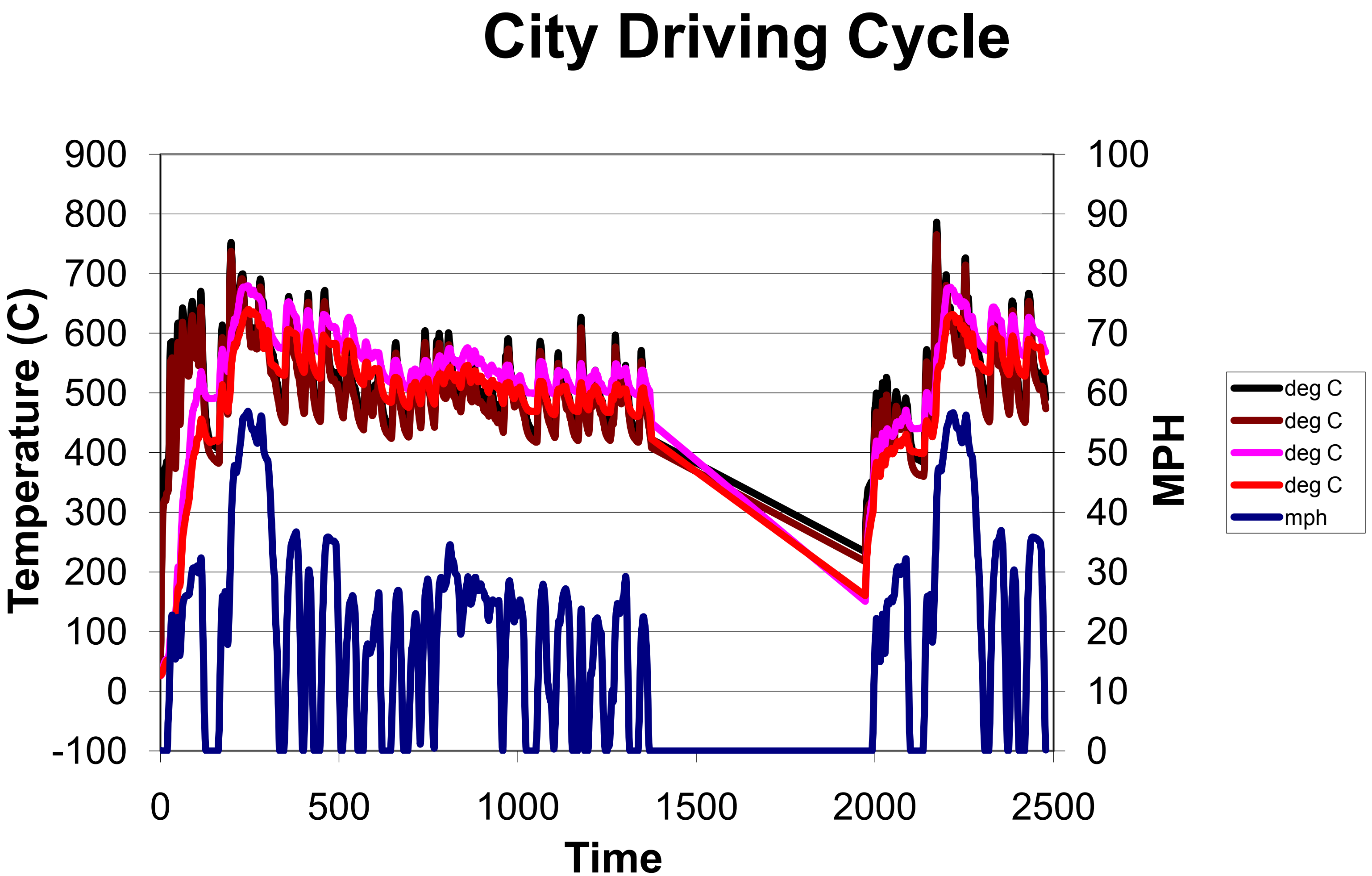
TE Automotive Waste Heat Recovery Vehicle Selection – Chevy Suburban



- The Suburban was selected as a test vehicle because it simplified the modifications and installation of the prototype.

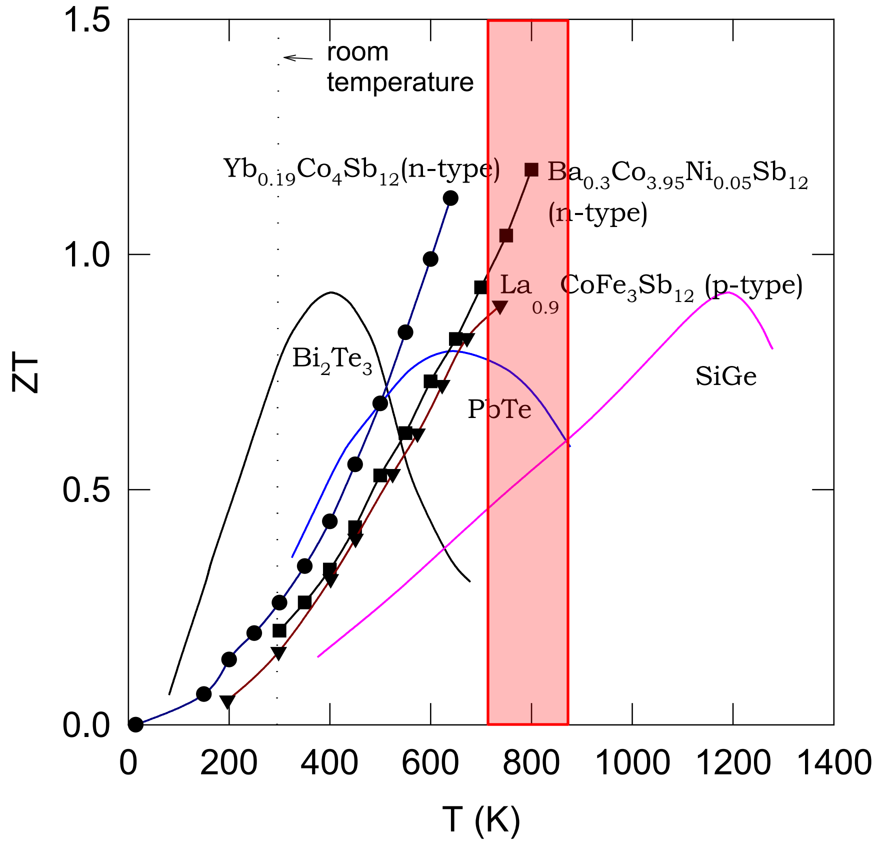
- Fuel efficiency improvement will be better in small, fuel efficient vehicles than in large vehicles because the electrical load in small vehicles is a larger portion of the engine output.

Chevy Suburban Exhaust Temperature



- ❑ The average exhaust temperature is around 500 – 600 °C

Skutterudites Have Excellent Thermoelectric Property in the Temperature Range of Interest



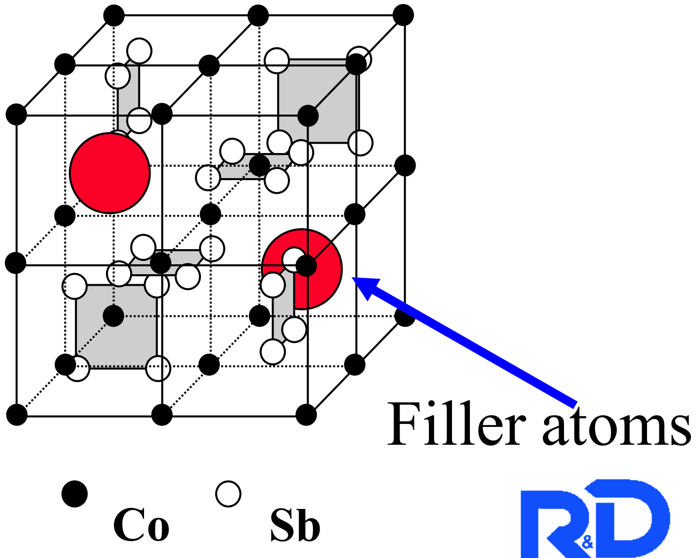
- ❑ **Prospective TE power generation materials for hot-side temperature near 800 K**
- ❑ **Both the n- and p-type exist – optimal for TE module construction**
- ❑ **The materials are mechanically strong (Wed. pm talk – James S. Salvador)**

Skutterudites 101

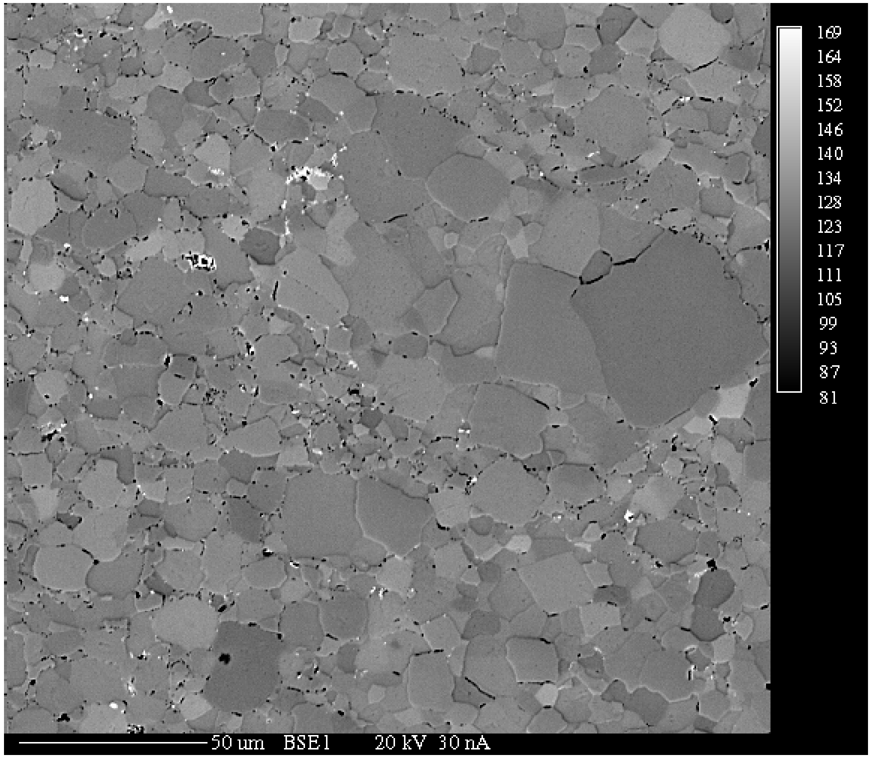
- $CoAs_3$ -based minerals found in region of Skutterud, Norway
- Compounds with the same crystal structure are known as “skutterudites”
- Filled skutterudites are electron-crystal-phonon-glass materials

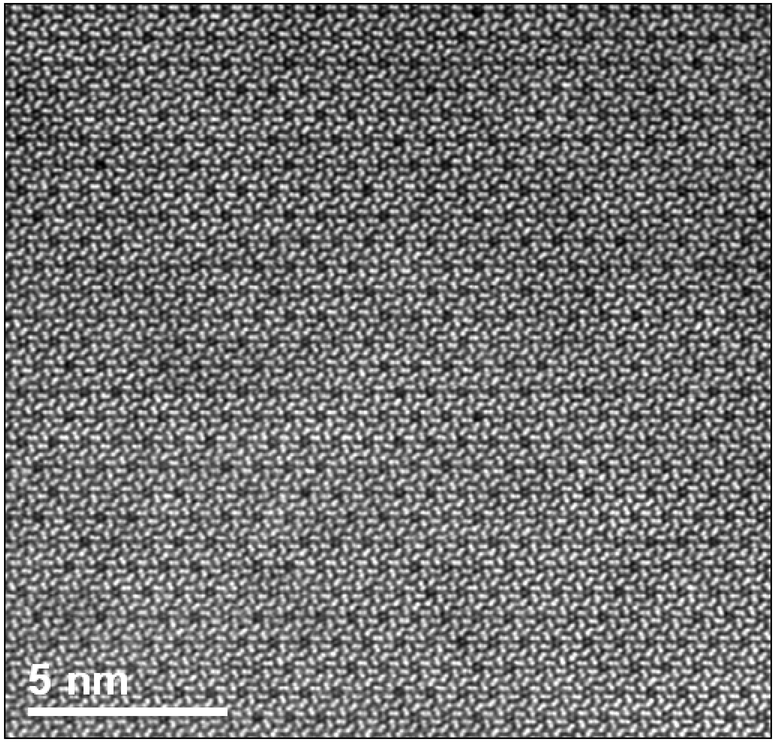
Skuterud gård, Modum

Co_4Sb_{12}



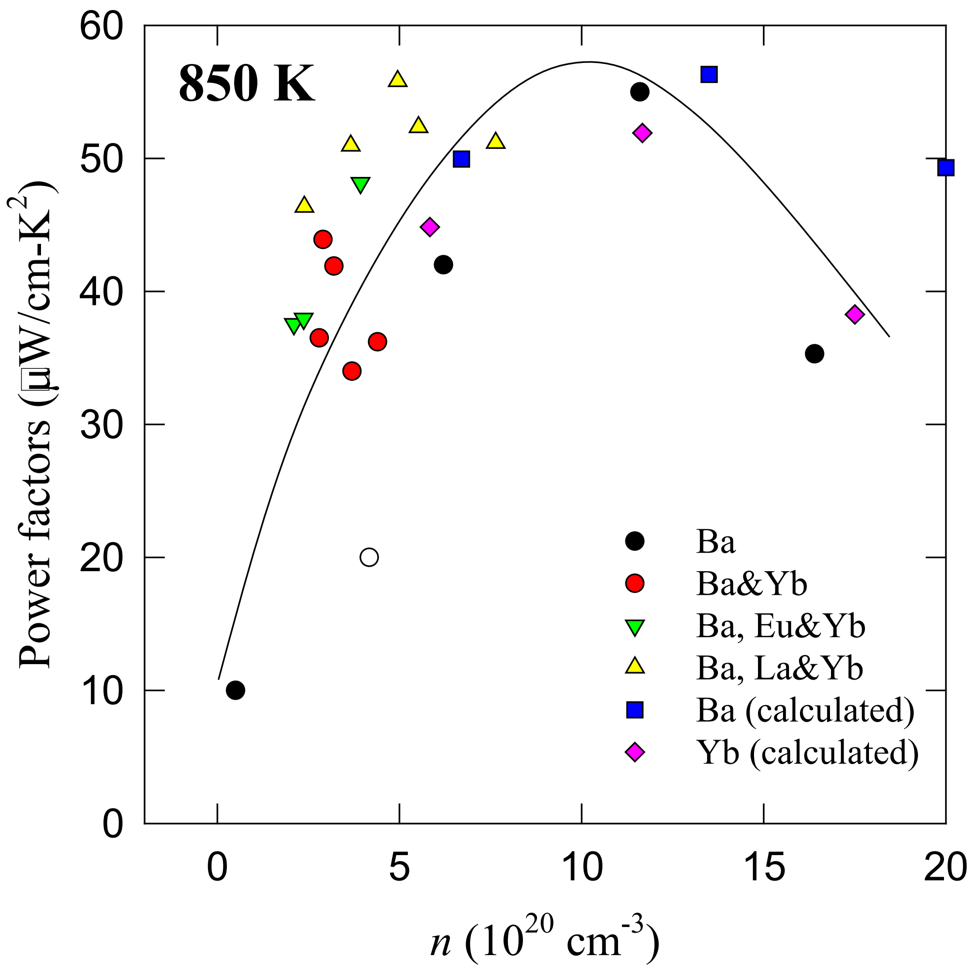
Structural Uniformity is Critical for Achieving Good Electrical Properties





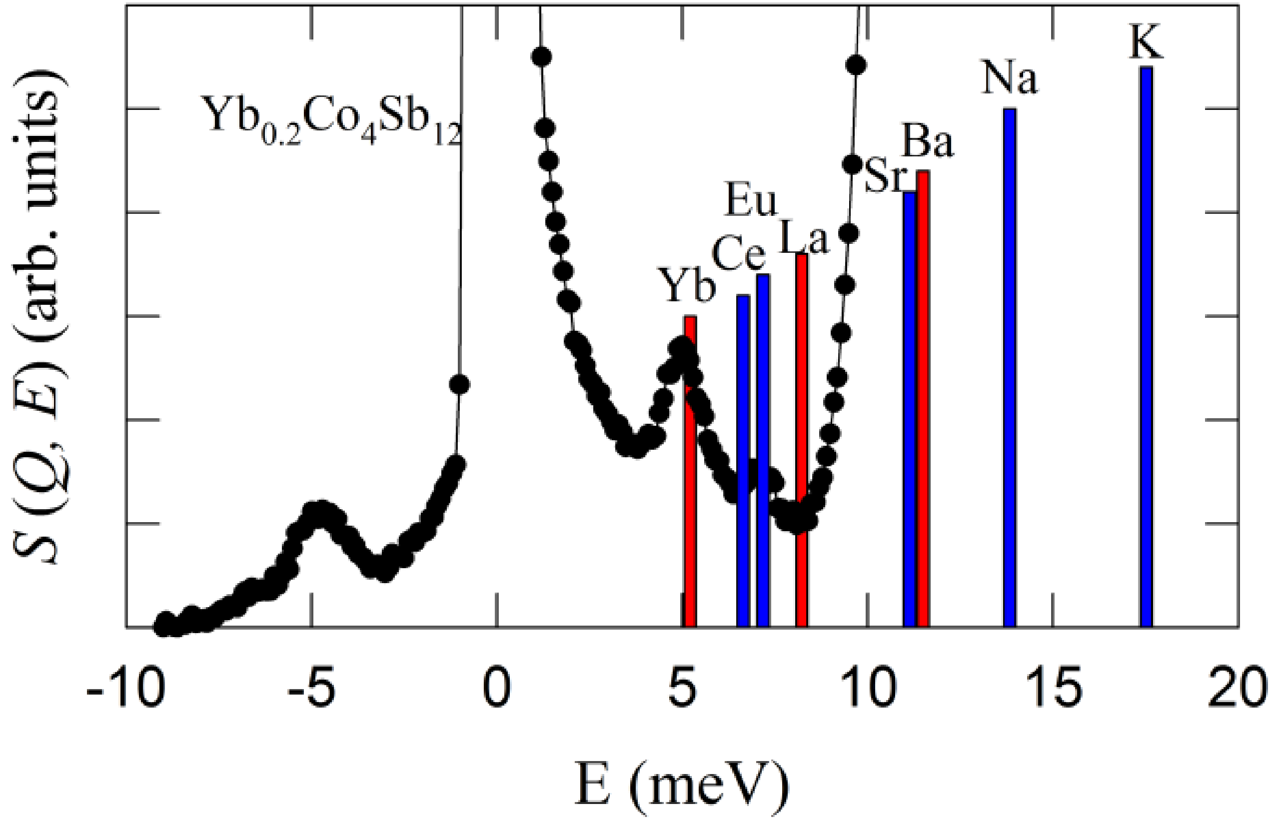
❑ Macroscopic backscattered electron image (left) and atomic-level high angle annular dark-field STEM (HAADF-STEM) along the [111] orientation (right) of $Ba_{0.08}La_{0.05}Yb_{0.04}Co_4Sb_{12}$

Very High Power Factor Values Achieved



❑ Power factor > 50 μW/cm-K^2 measured in a large carrier concentration range between 5 and 15 × 10^{20} cm^{-3}

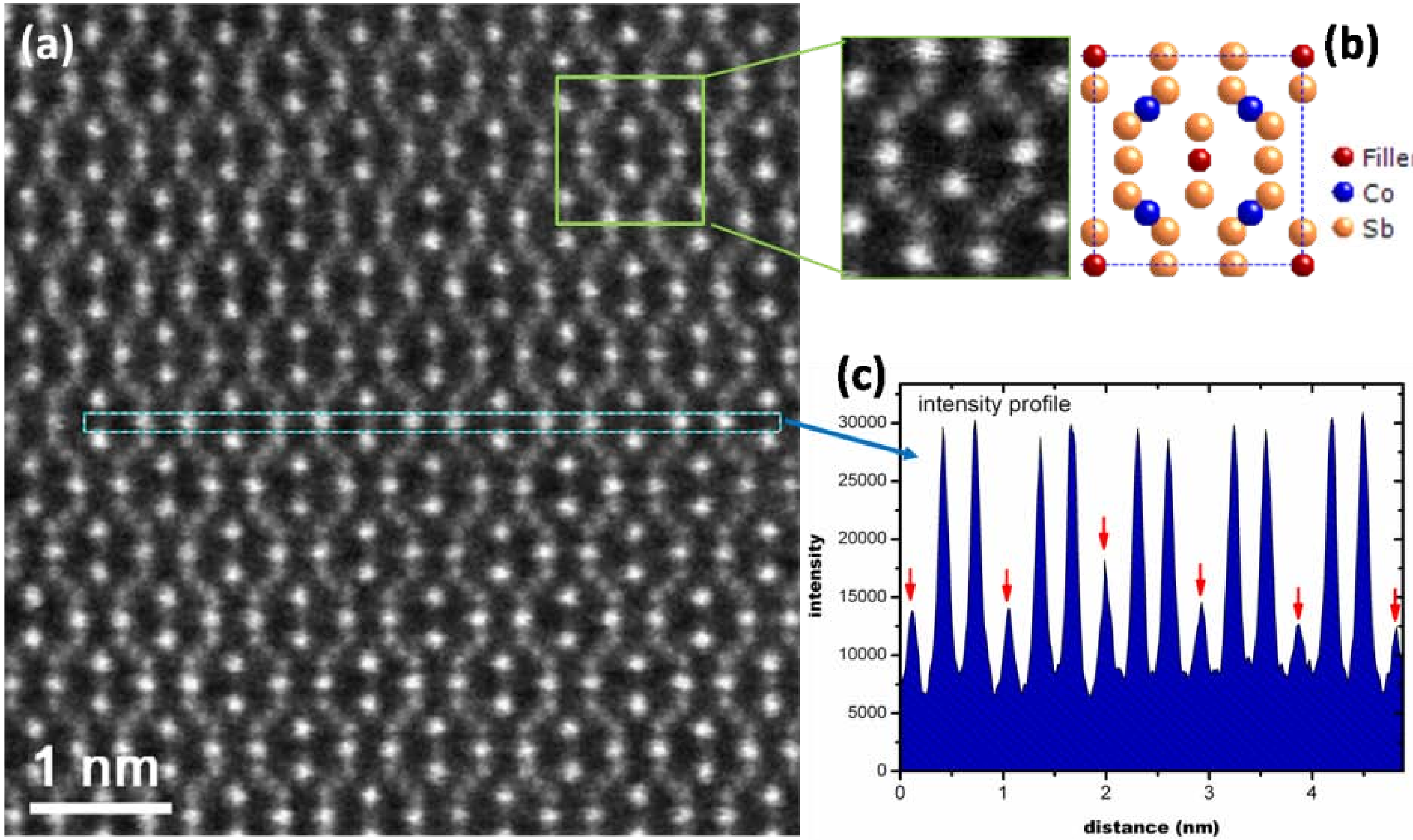
Multiple-Element-Filling Concept



- ❑ Skutterudites can be designed to achieve very low lattice thermal conductivity by introducing multiple, non-overlapping phonon resonant center

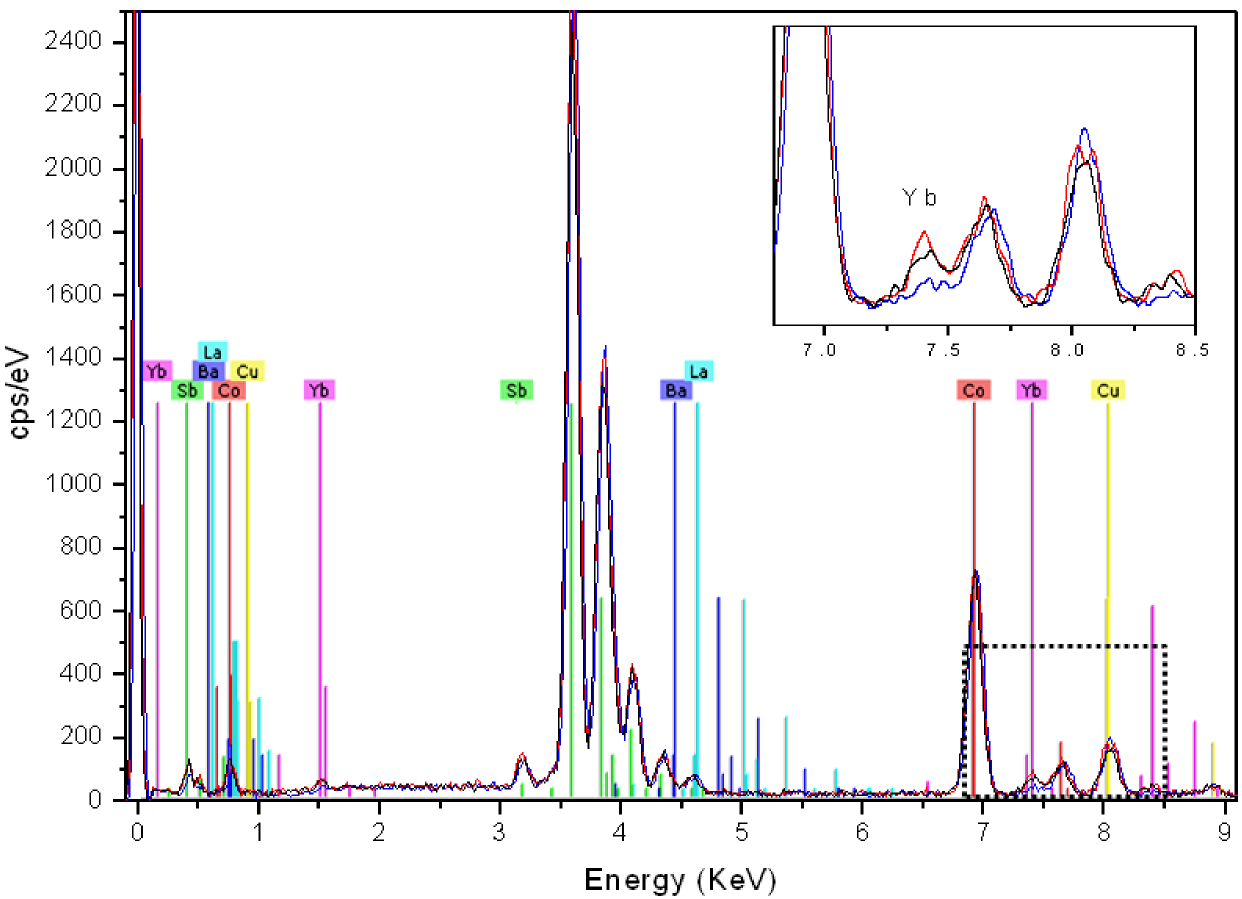
Yang, *et al.*, *Appl. Phys. Lett.* **90**, 192111, 2007; Shi, *et al.*, *Appl. Phys. Lett.* **92**, 182101, 2008

HAADF-STEM Image of $Ba_{0.08}La_{0.05}Yb_{0.04}Co_4Sb_{12}$ Along the [001] Orientation



- ❑ In the [001] direction, one can identify filler-only atomic columns
- ❑ Fillers are randomly distributed in the crystallographic voids

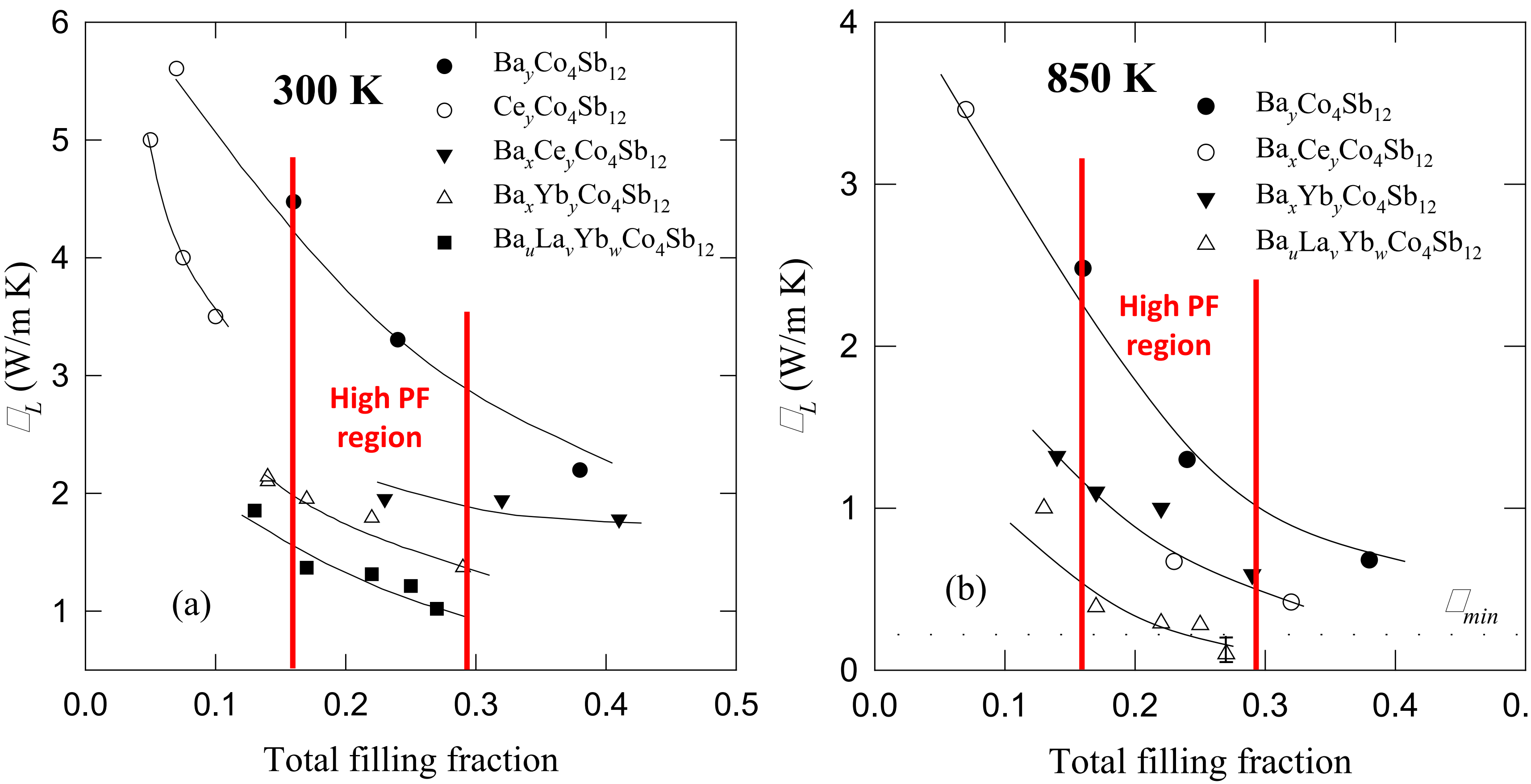
EDS Spectra Randomly Acquired from Filler Columns



Cu signal is from the TEM Cu supporting grid

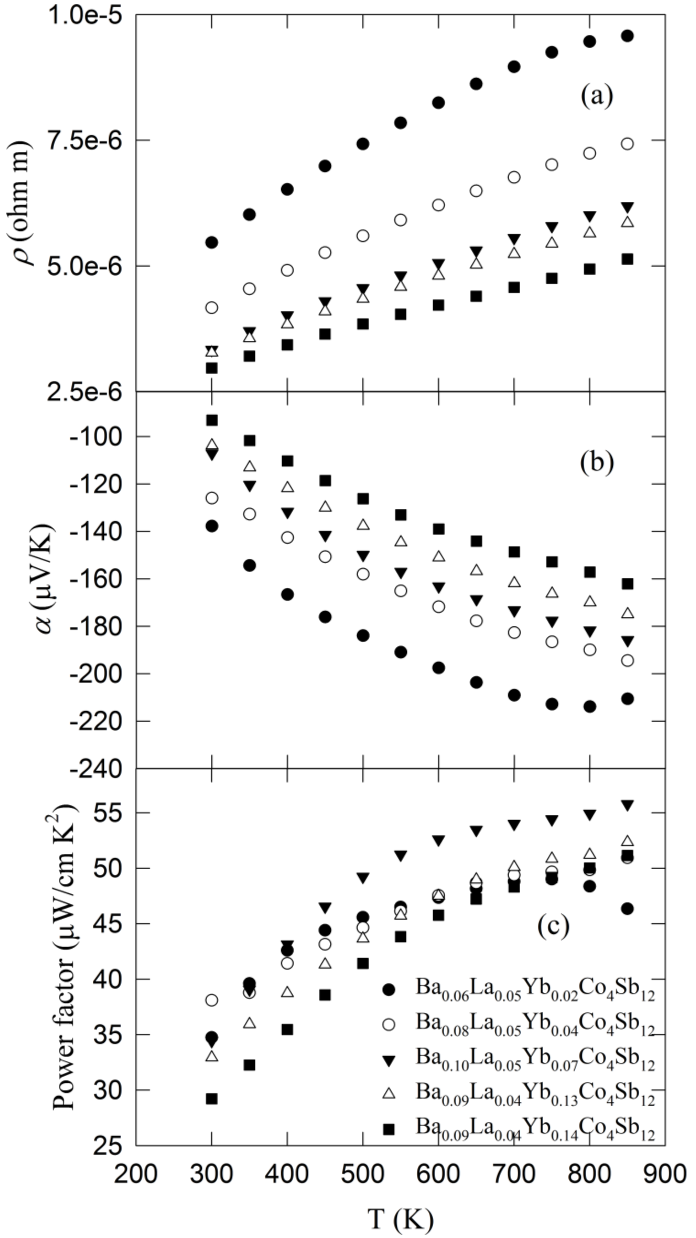
- ❑ The e-beam size is approximately 0.15-0.2 nm
- ❑ The distribution of Yb (and other fillers) are random

Lattice Thermal Conductivity Reduction from Single- to Triple-element-filled skutterudites

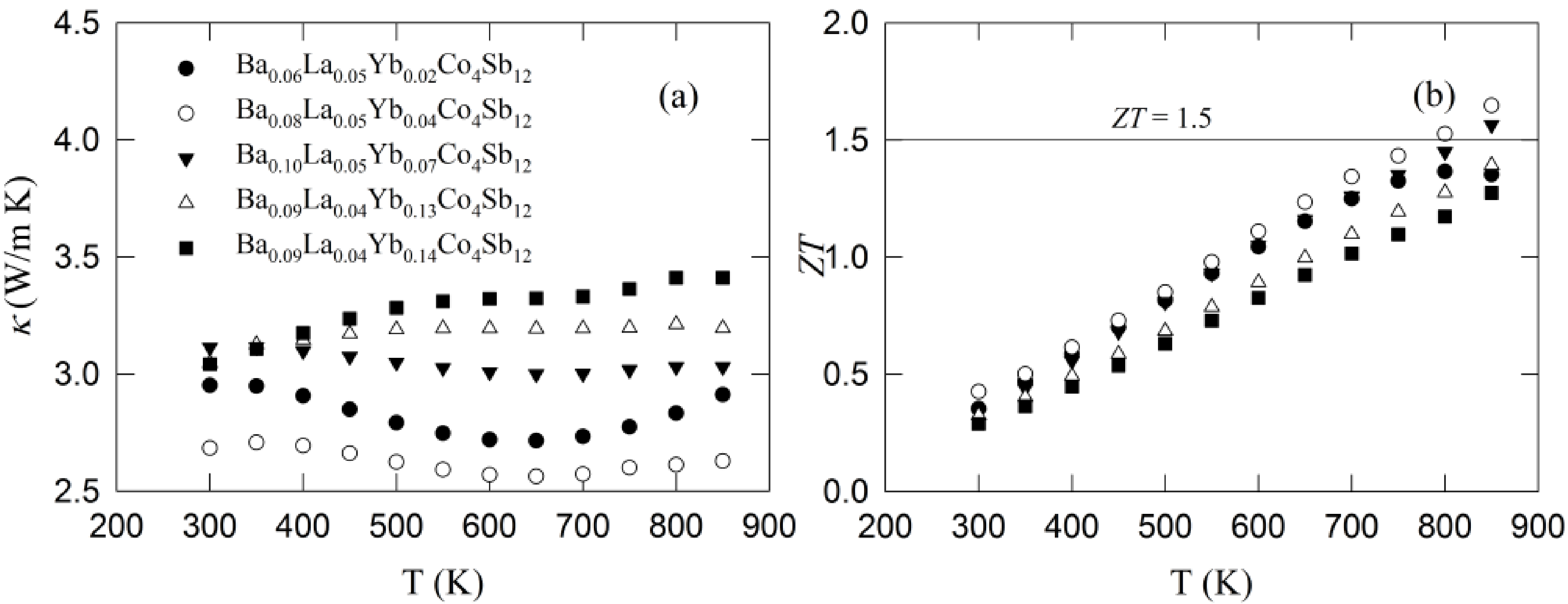


- Minimum lattice thermal conductivity is achieved at elevated temperatures

Very High Power Factor Values in a Wide T Range

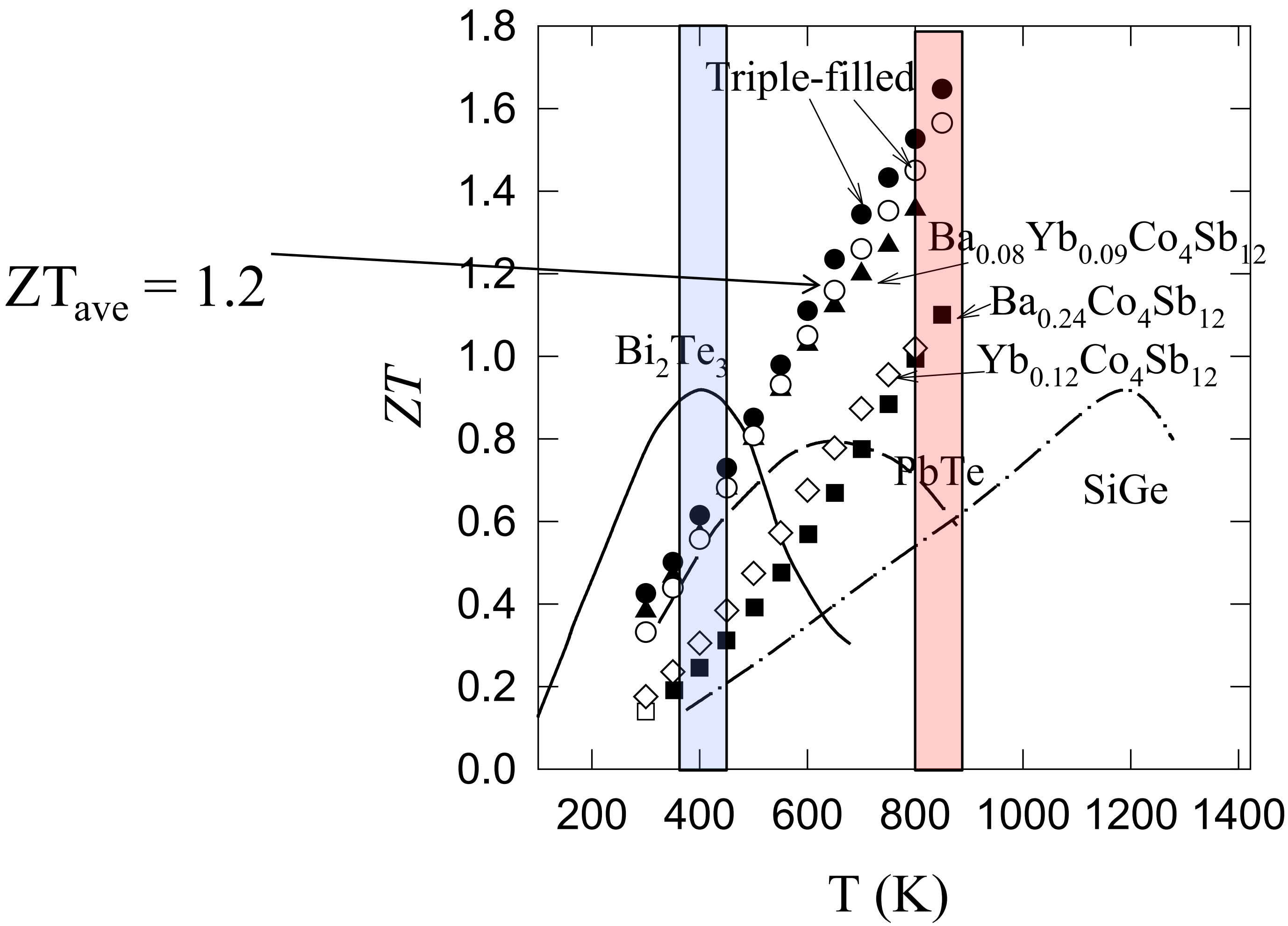


ZT of $Ba_uLa_vYb_wCo_4Sb_{12}$



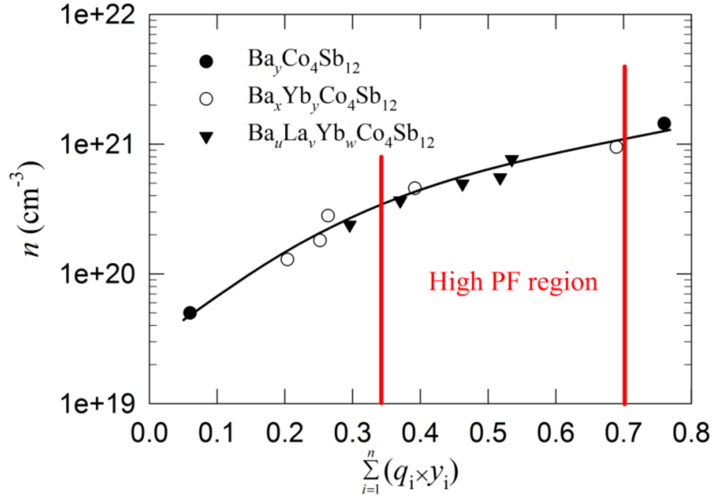
- ❑ Multiple-filled skutterudites possess some of the highest ZT values reported for bulk TE materials
- ❑ ZT_{max} = 1.7 at 850 K

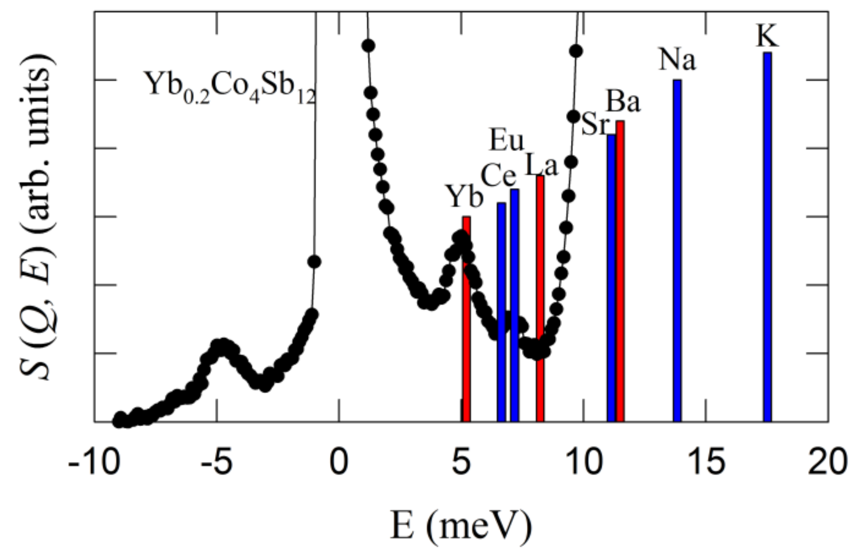
Single-, Double-, to Triple-filled



1. X. Shi, et al. Appl. Phys. Lett. **92**, 182101 (2008)
2. X. Shi, et al., submitted (2009)

Key Take-Aways





- ❑ Ba, Yb, and La should not be the only combination that gives rise to high ZT
- ❑ High PF values unchanged from single-, double-, to triple-element-filled n-type skutterudites
- ❑ The optimum carrier concentration corresponds to ~ 0.35-0.75 e/fu, which means that composition can be designed using the nominal valence state of the filler ions

Conclusions

- ❑ Multiple-element-partially-filled skutterudites are amongst prospective n-type materials for automotive exhaust waste heat recovery applications

- ❑ The skutterudites-based TE generator can be further improved by optimizing the p-type materials

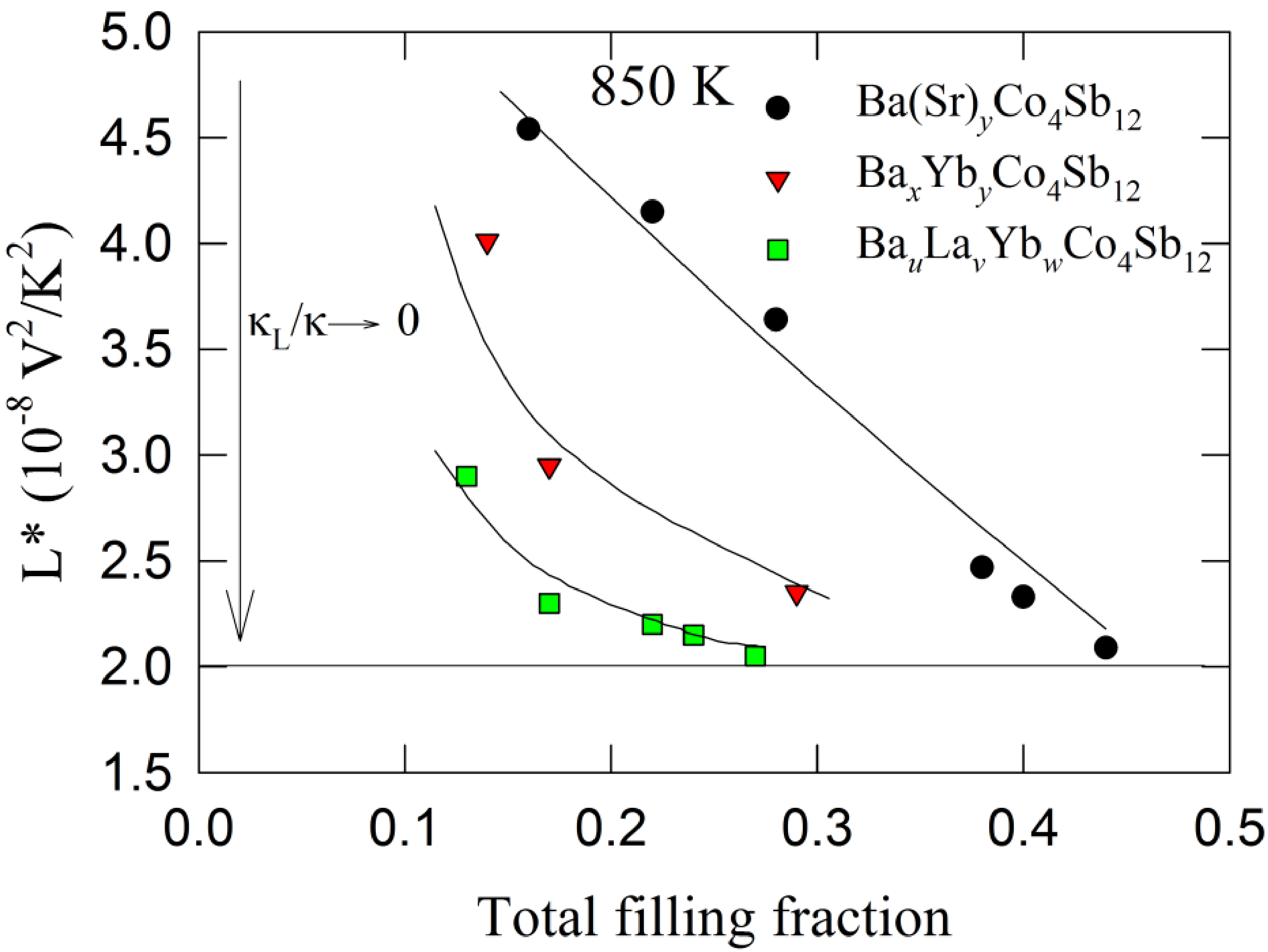
- ❑There are plenty of engineering to be done
    - strength improvement
    - contacts/interconnects
    - heat exchanger
    - power electronics

Acknowledgement

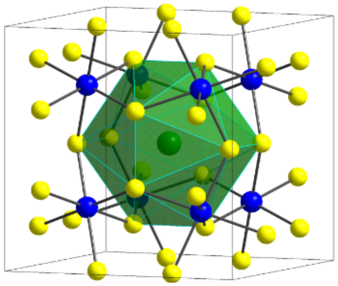
- GM and DOE for support under corporate agreement DE-FC26-04NT42278
- James R. Salvador, Xun Shi, Jung Young Cho, Gregory P. Meisner, Mike Reynolds (GM); Wenqing Zhang, Lidong Chen (SIC); Hsin Wang, M. Chi (ORNL); John Copley, Jack Rush (NCNR).
- John Fairbanks and Francis Stabler for many useful discussions

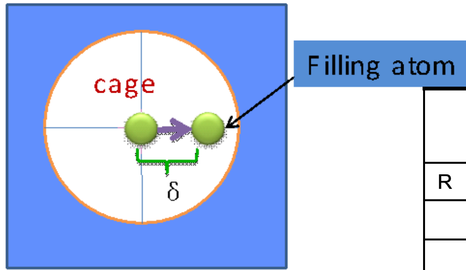
Thank You !

Lorentz Number



Filler Atoms in Skutterudites Rattle with Different Frequencies - Theory





Small displacement δ of the filler from it equilibrium x will lead to an increase of the total energy of the system.

$$E(x+\delta) = \underbrace{E(x) + \frac{1}{2}\ddot{E}(x)\delta^2}_{\text{harmonic term}} + \underbrace{\frac{1}{6}\dddot{E}(x)\delta^3 + \cdots}_{\text{anharmonic term}}$$

In a harmonic approximation, $\ddot{E}(x)$ is the spring constant.

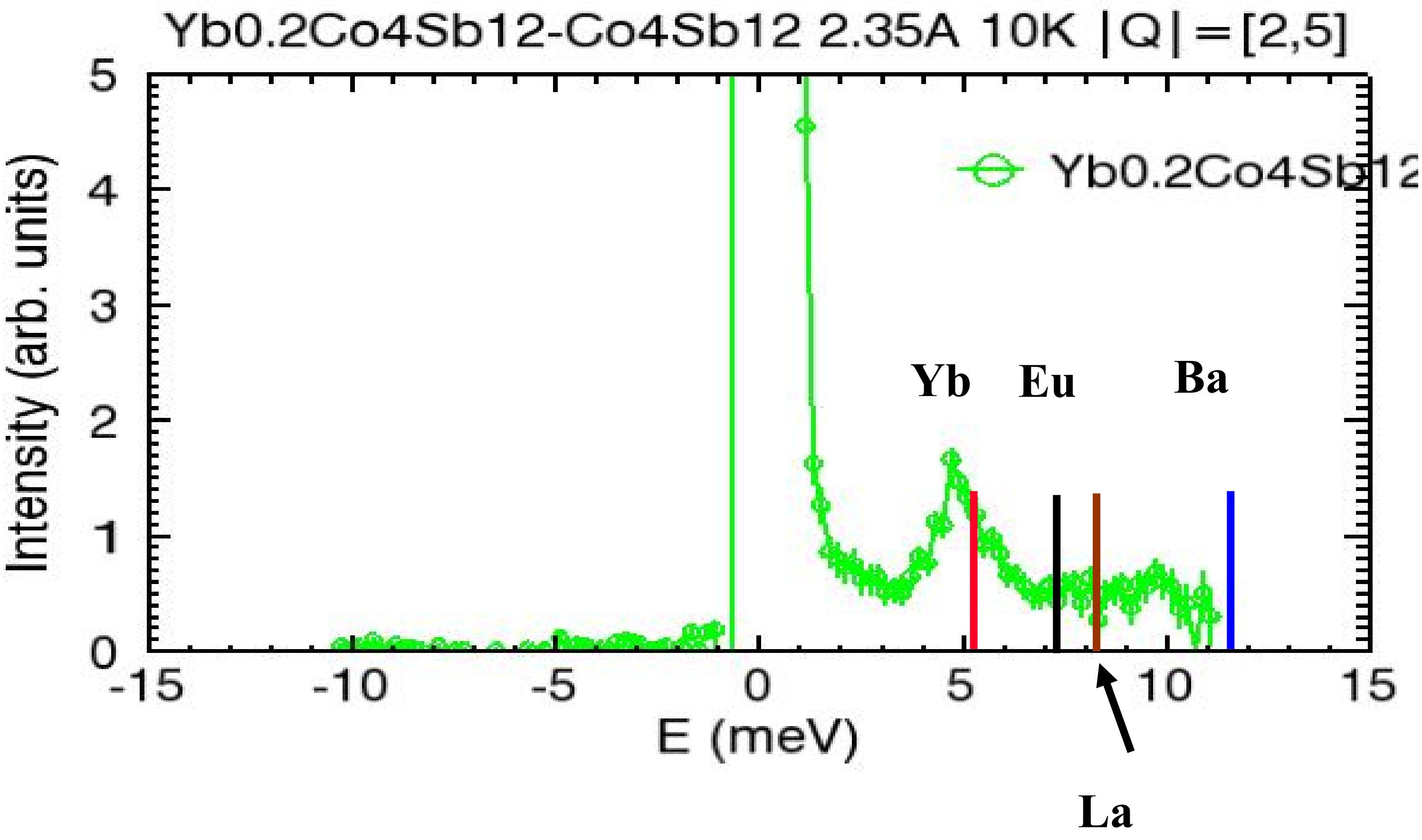
$$\omega_0 = \sqrt{\frac{\ddot{E}(x)}{m}}$$

		[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

- Multiple-element filling will scatter a broad range of lattice phonons, lower thermal conductivity, and improve ZT[1-3]

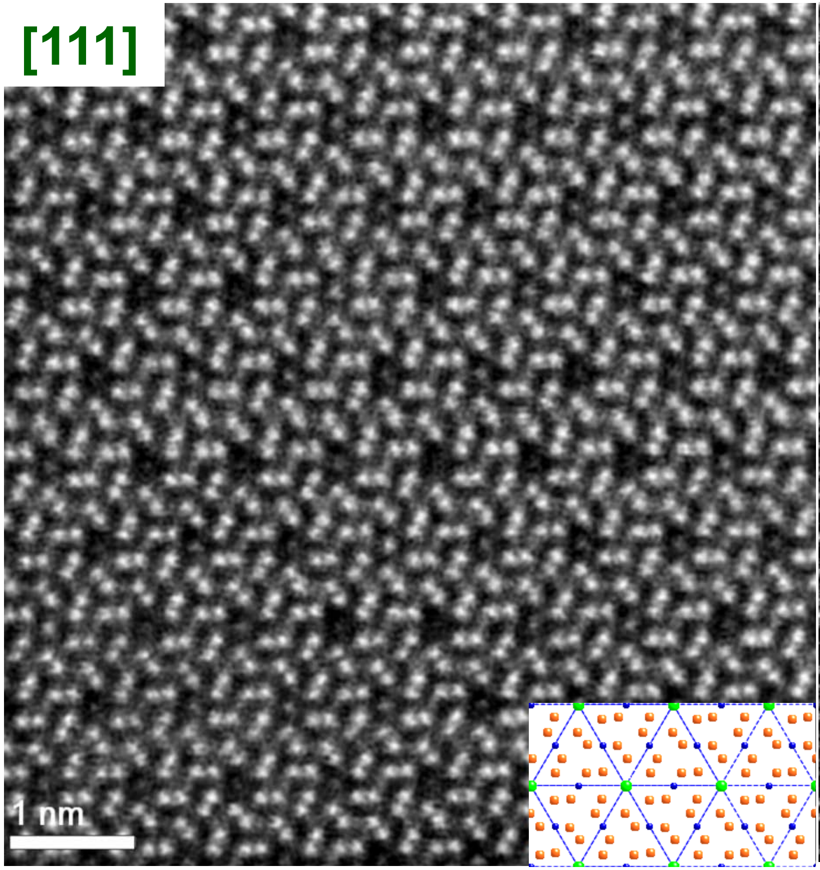
1. Shi, X., Zhang, X., Chen, L. D., and **Yang, J.**, *Phys. Rev. Lett.* **95**, 185503, 2005.
2. **Yang, J.**, Zhang, W., Bai, S. Q., Mei, Z., and Chen, L. D., *Appl. Phys. Lett.* **90**, 192111, 2007.
3. Shi, X., Kong, H., Li, C.-P., Uher, C, **Yang, J.**, Salvador, J. R., Wang, H., Chen, L., and Zhang, W., *Appl. Phys. Lett.* **92**, 182101, (2008)

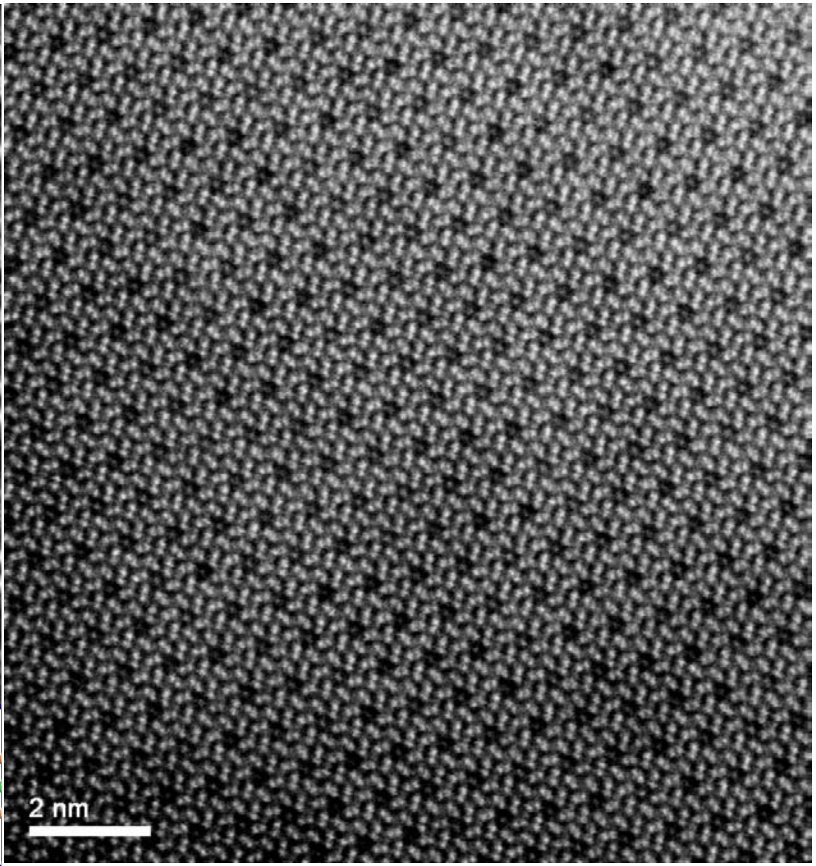
Phonon DOS Measured by Inelastic Neutron Scattering – Experiment



• Calculated resonant phonon frequencies are experimentally validated

STEM Images of the Triple-Filled Skutterudites





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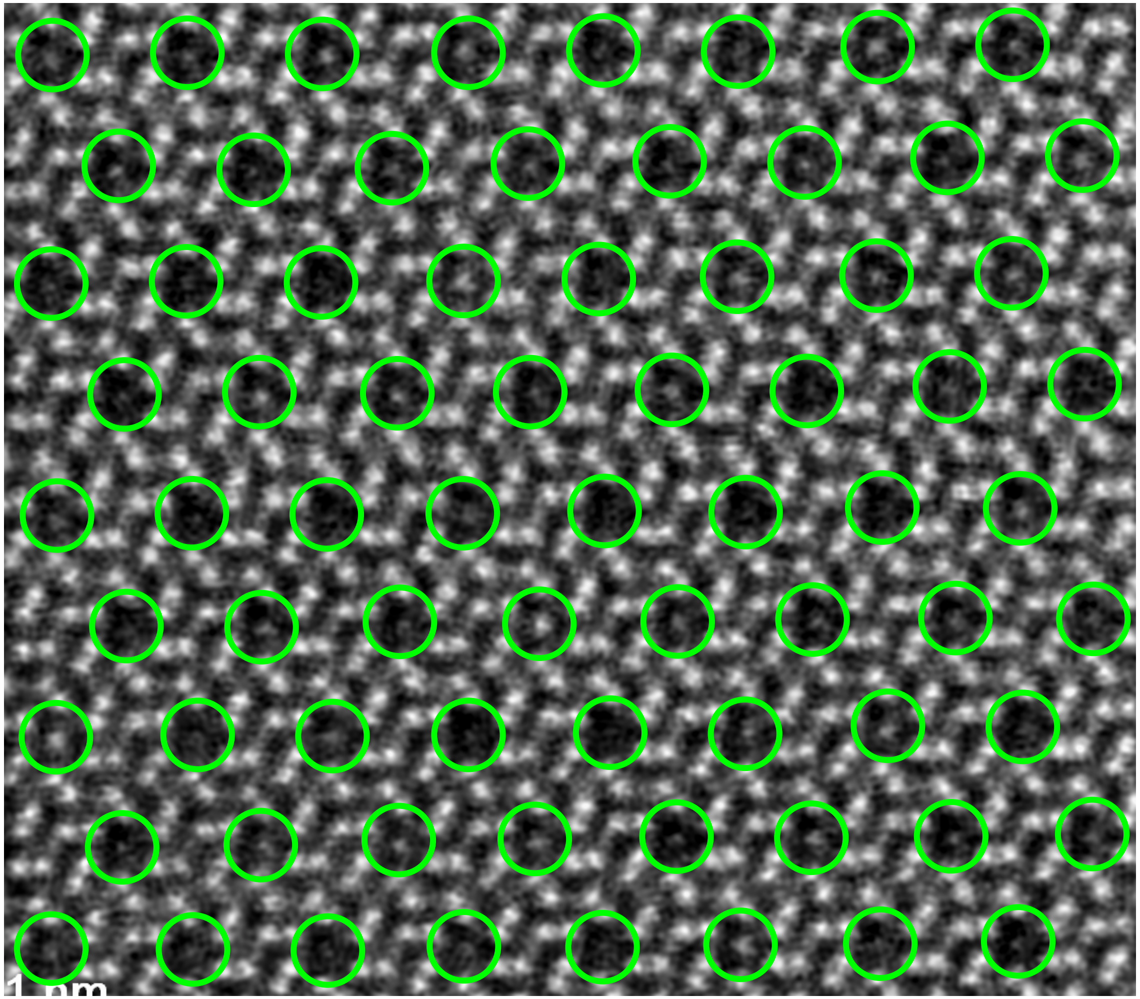

Phonon DOS Measurement – Inelastic Neutron Scattering