

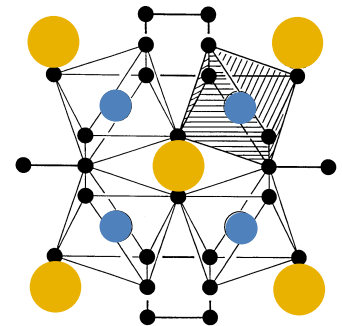
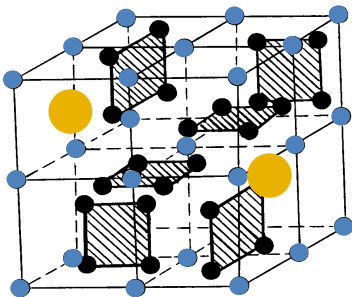


Recent Progress in the Development of N-type Skutterudites

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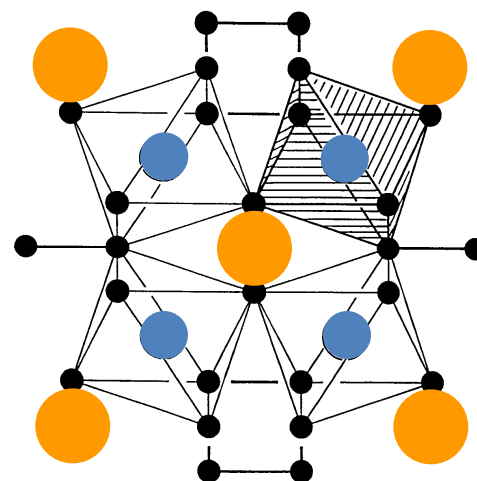
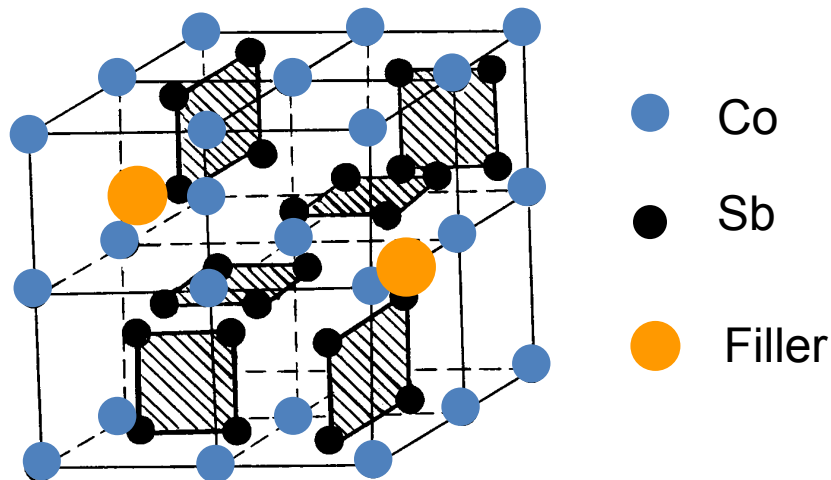
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September 29 – October 2, 2009
San Diego, CA



Skutterudite compounds

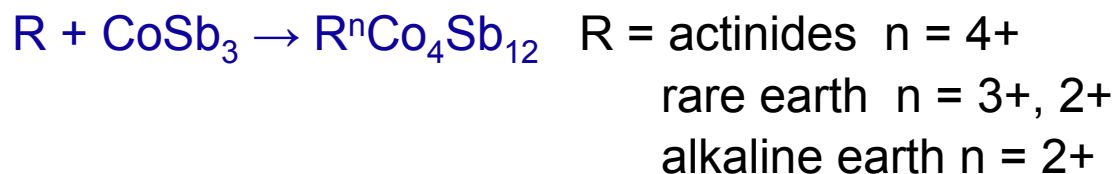
Chemical formula MX_3 $M = \text{Co, Rh, Ir}$ $X = \text{P, As, Sb}$

Cubic structure with eight MX_3 groups in the unit cell \Rightarrow 32 atoms/unit cell

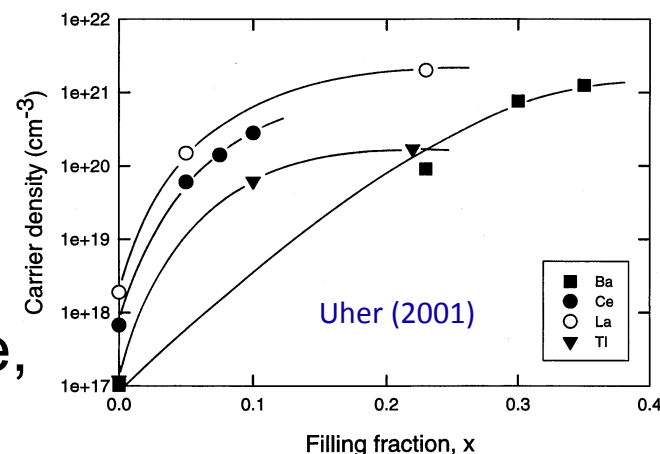


Cages can be filled with foreign ions \Leftrightarrow **Filled skutterudites** Jeitschko (1977)

Filler species donate electrons



Filling drives skutterudites strongly n-type,
 limiting occupancy of voids.



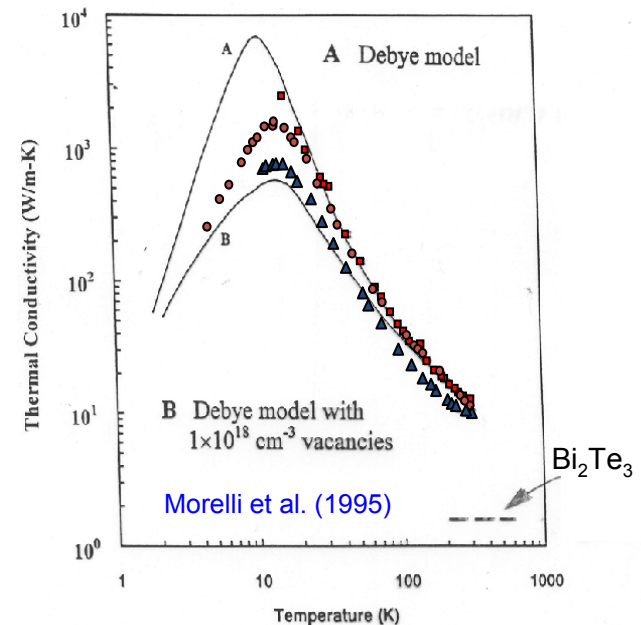
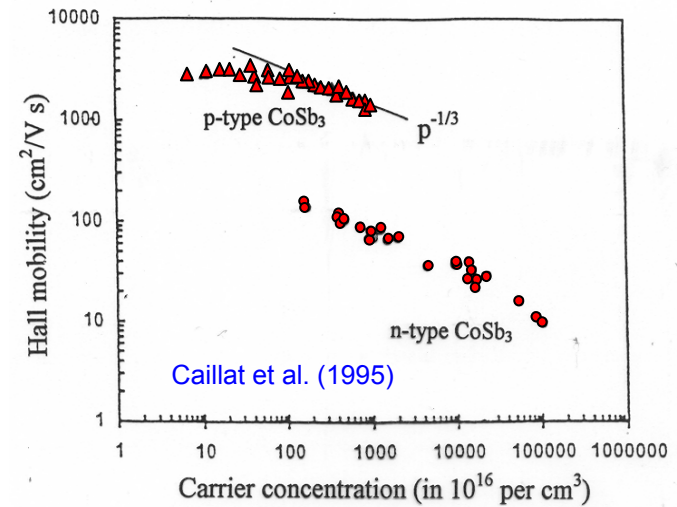


Binary skutterudites

Possess some of the highest mobilities of all bulk semiconductors.

Unfortunately, thermal conductivity is far too high ($\kappa \sim 10$ W/m-K for CoSb_3 at 300K).

Not suitable as thermoelectrics!





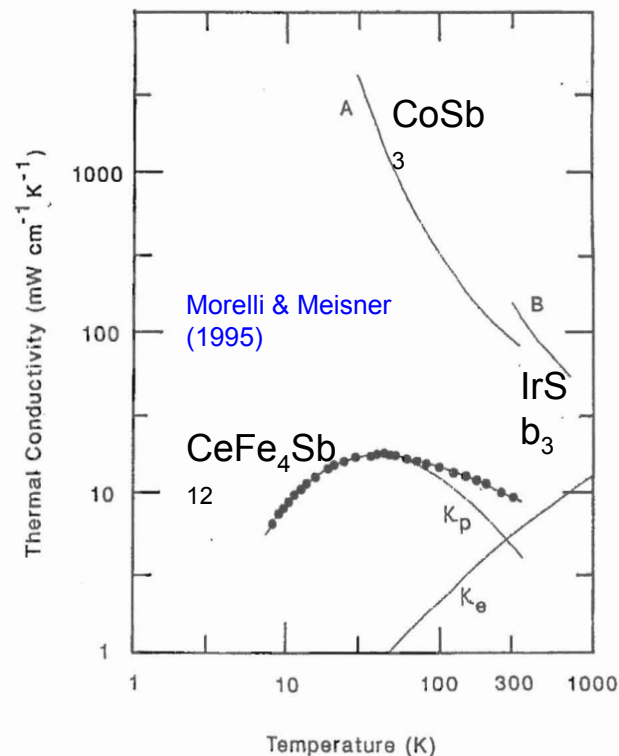
Glen Slack in 1994 – PGEC Paradigm

Filled skutterudites should be interesting because:

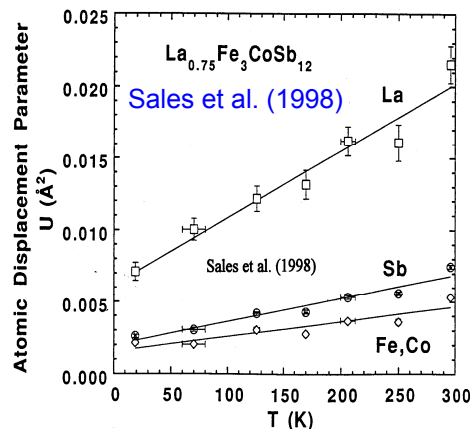
- Fillers should be loosely bonded to the cage atoms.
- Fillers should have large atomic displacements.
- They should act as independent oscillators (“rattlers”).
- Interaction of rattlers with the normal modes should lower κ_L .
- Rattlers should not greatly affect excellent electronic properties.



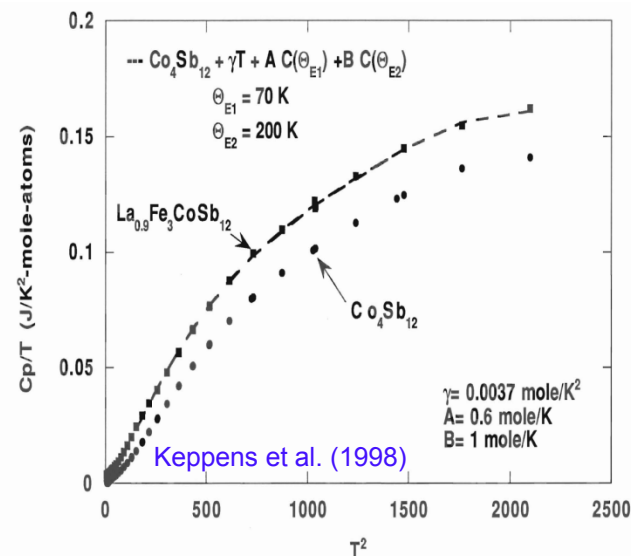
Strong initial experimental support for the ideas of Slack



Filled skutterudites have an order of magnitude lower thermal conductivity!



Indeed, atomic parameters of “rattlers” are much larger than of other atoms.



Perhaps the most convincing evidence for “rattling” of fillers comes from the two Einstein oscillator model of Keppens et al. (1998) based on: inelastic neutron scattering and low temperature specific heat.



Resent Challenges to the “Rattling” Theory

Koza et al., ICT-2006 (Vienna) & Nature Materials 7, 805 (2008)

Classical “rattler” should have the following properties:

- Vibrational energy should be independent from the wave-vector transfer ($d\omega_q/dq=0$).
- Lack of phase coherence of the vibrational motion .

Koza et al. argued that none of these criteria were tested for so far.

Only techniques simultaneously probing $\hbar\omega(\mathbf{Q})$ and $\hbar\mathbf{Q}$ can provide answer.

One such technique is High Resolution Time-of-Flight Neutron Scattering.

The authors used $\text{CeFe}_4\text{Sb}_{12}$ (i.e., a fully filled skutterudite)

- Vibrational modes of Ce fillers are coherently coupled with atoms of the host.
- Presence of van Hove singularities in the phonon spectrum giving $v_g=d\omega_q/dq=0$.
- Phonon transport hindered by Umklapp processes.

In Vienna I asked what if the skutterudite is only partly filled?

Just completed inelastic neutron scattering studies by Dr. Yang and his group on $\text{RCo}_4\text{Sb}_{12}$ contrast the work of Koza et al. and support the PGEC concept.

Regardless of the physical origin, the fact remains that filling the skutterudite structure is the essential step to produce an efficient thermoelectric material.



Status of n-type skutterudites

- Fillers considered early were mostly rare earths Ce^{3+} and La^{3+} , low filling fraction, particularly for Ce ($y < 0.1$), $ZT \sim 0.6$ at 800K.
- **Anno et al.** (2000) and **Nolas et al.** (2000) tried Yb, a mixed valence ion, larger filling fraction ($y \sim 0.25$), $ZT \sim 1.1$ at 800K.
- **Chen et al.** (2001) introduced alkaline earths, notably Ba, strictly divalent ions, large filling fraction ($y \sim 0.45$), $ZT \sim 1.2$ at 800K.
- **Shi et al.** (2005) & (2007) developed theory for calculation of filling fraction limits.
- **Yang et al.** (2007) calculated resonant phonon frequencies for filler ions.
- **Shi et al.** (2008) synthesized double-filled $\text{Ba}_x\text{Yb}_y\text{Co}_4\text{Sb}_{12}$, a large contrast in resonant frequencies of Ba and Yb, $ZT = 1.36$ at 800K.
- **Li et al.** (2008) used a rapid melt-spinning technique on $\text{Ba}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ that cuts synthesis time and forms nanostructure resulting in $ZT=1.3$ at 800K.
- **Li et al.** (2009) observed *in-situ* forming nanostructured InSb phase in $\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12}$ prepared by melt-spinning & spark plasma, $ZT = 1.43$ at 800K.
- **Shi et al.** (2009) triple-filled skutterudite measured recently, $ZT = 1.7$ at 800K.

Excellent progress, what else can be done?



Try partial compensation to achieve high ZT in n-type skutterudites

In 1997, we noted ([Morelli et al. PRB 56](#)) that a partial substitution of Co by Fe leads to a marked **reduction** in the thermal conductivity of skutterudites.

A surprising observation since atomic mass and ionic radius of Co and Fe are similar.

We rationalized this observation ([Meisner et al., PRL80](#)) by picturing a fractionally filled skutterudite as a solid solution of fully filled and unfilled end members, i.e., as

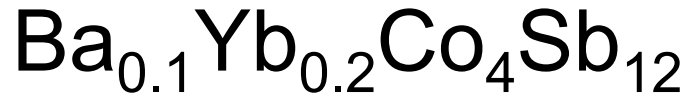


Low thermal conductivity is now readily understood: it is not due to mass fluctuation scattering between Fe and Co but between R and \uparrow (vacancy) and this represents a 100% mass difference!

Of course, Fe substitution for Co is the main route to making **p-type skutterudites**. But perhaps a small amount of Fe on the sites of Co might lower thermal conductivity to a greater extent than the compensating effect of Fe would have on the magnitude of the Seebeck coefficient of **n-type skutterudites**?



To test the idea, 3 double-filled compounds synthesized:



a reference sample



partly compensated sample



partly compensated sample

Fe²⁶

2-8-14-2
3d⁶4s²

Co²⁷

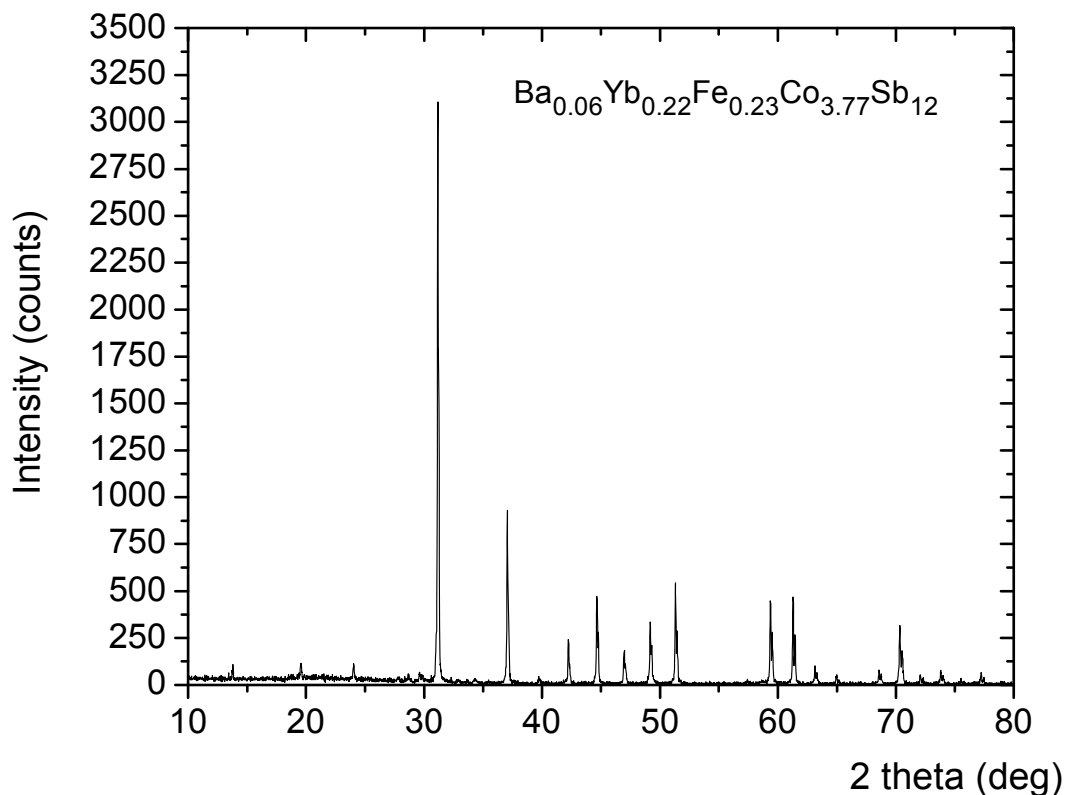
2-8-15-2
3d⁷4s²

The presence of Fe: ● expands the FFL and
● **lowers thermal conductivity**



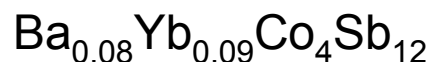
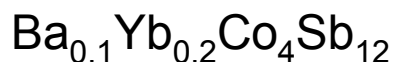
Synthesis

- Peritectic system \Rightarrow solid state reaction.
- Ba: 99.9%; Yb: 99.9%; Co: 99.998%; Fe: 99.998% Sb: 99.9999%
- Stoichiometric amounts of elements weighed in a glove box.
- Sealed in a carbon-coated quartz tube under vacuum.
- Melted at 1100°C for 10 hours.
- Annealed at 840°C for one week and quenched.
- Ingots crushed, pressed into pellets and further annealed for 1 week.
- Crushed and compacted by SPS into 1/2-inch diameter cylinders.
- XRD indicates single-phase skutterudites.



Nominal Composition

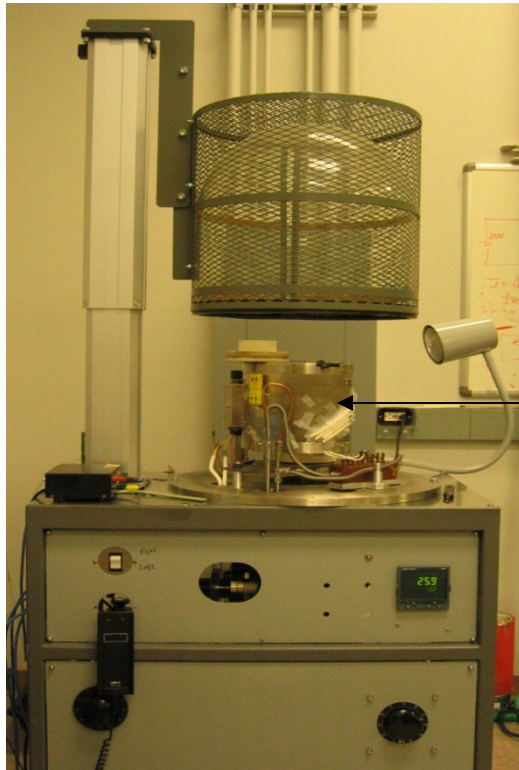
Actual Composition (EPMA)



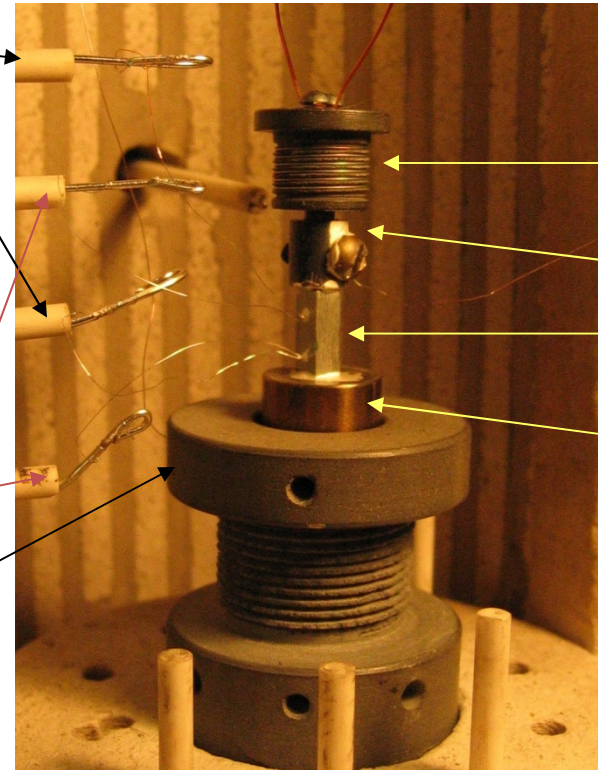


Property measurements

Resistivity and Seebeck coefficient



Pt electrodes
Bell jar
Cylindrical oven
Pt-Rh electrodes
Ceramic support



wire-wound heater
tungsten sample
tungsten

Fully computerized system operating to 1300K under vacuum or Ar gas.
Pt vs. Pt/Rh thermocouples, Pt legs used for Seebeck probes.
Probes attached with Ag paste ($T < 800\text{K}$) or inserted in tiny holes with graphite paste.
Tungsten electrodes for current injection.



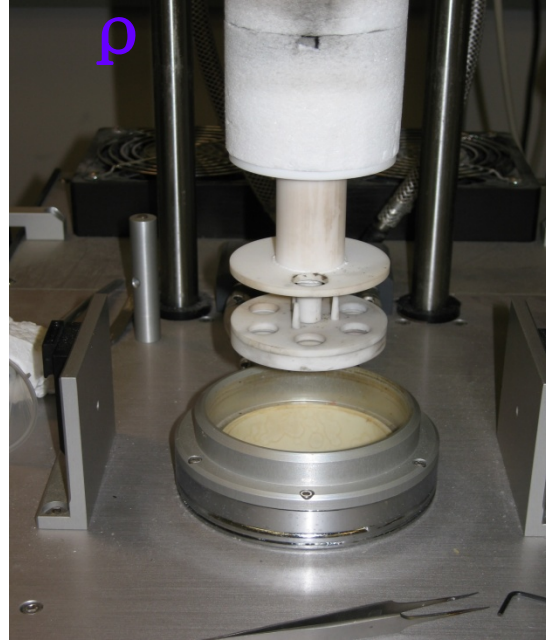
Property measurements

Thermal conductivity

$$\kappa = D \times C_p \times \rho$$



FlashLine 5000 apparatus from Anter Corp.
Temperature range 300K – 1800K
Six sample carousel
Fully automated operation

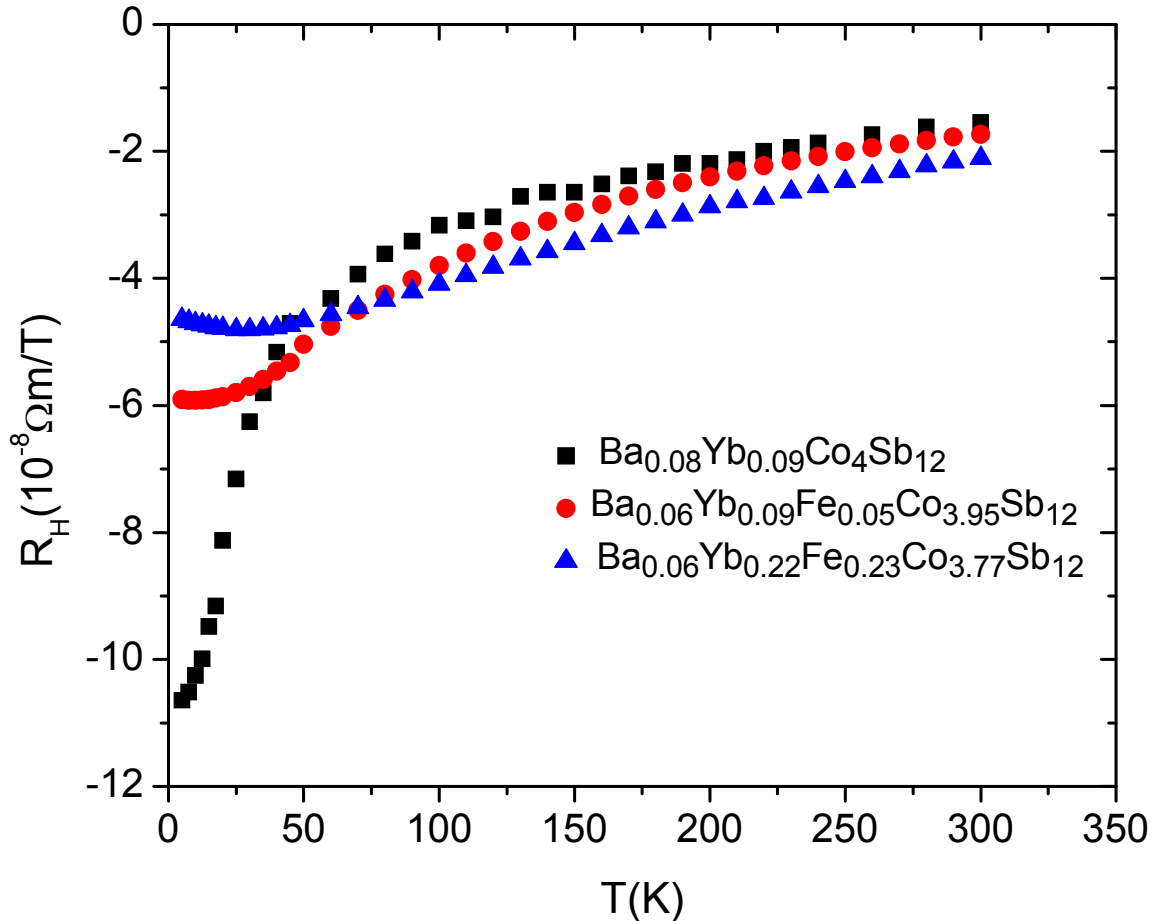


DSC 404C Pegasus® (Netzsch)
Temperature range 300K-1800K
Fully automated operation



Hall coefficient

Low frequency ac-technique in the field of 1T

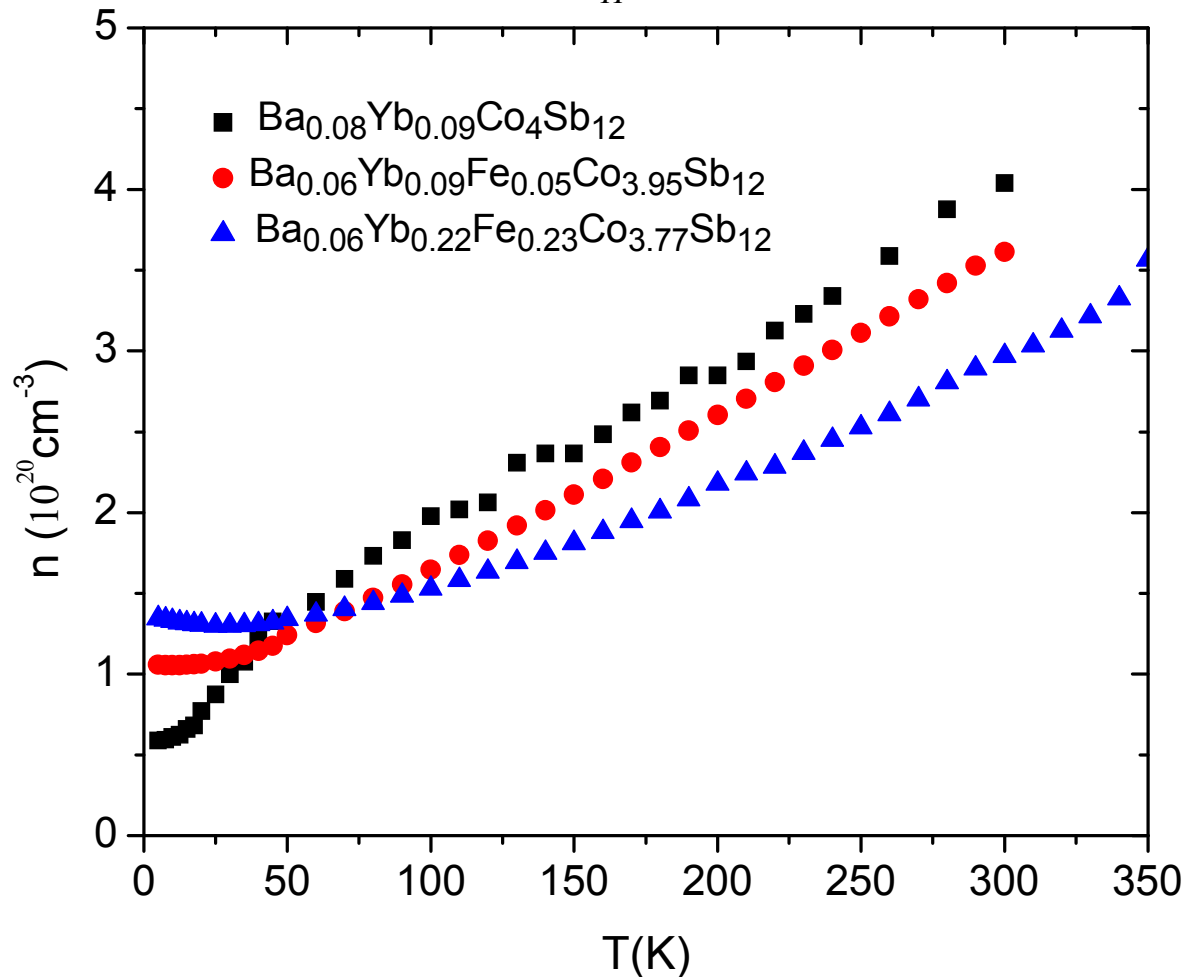


Increasing Fe content $\Rightarrow |R_H|$ increases \Rightarrow density of electrons decreases.



Density of electrons

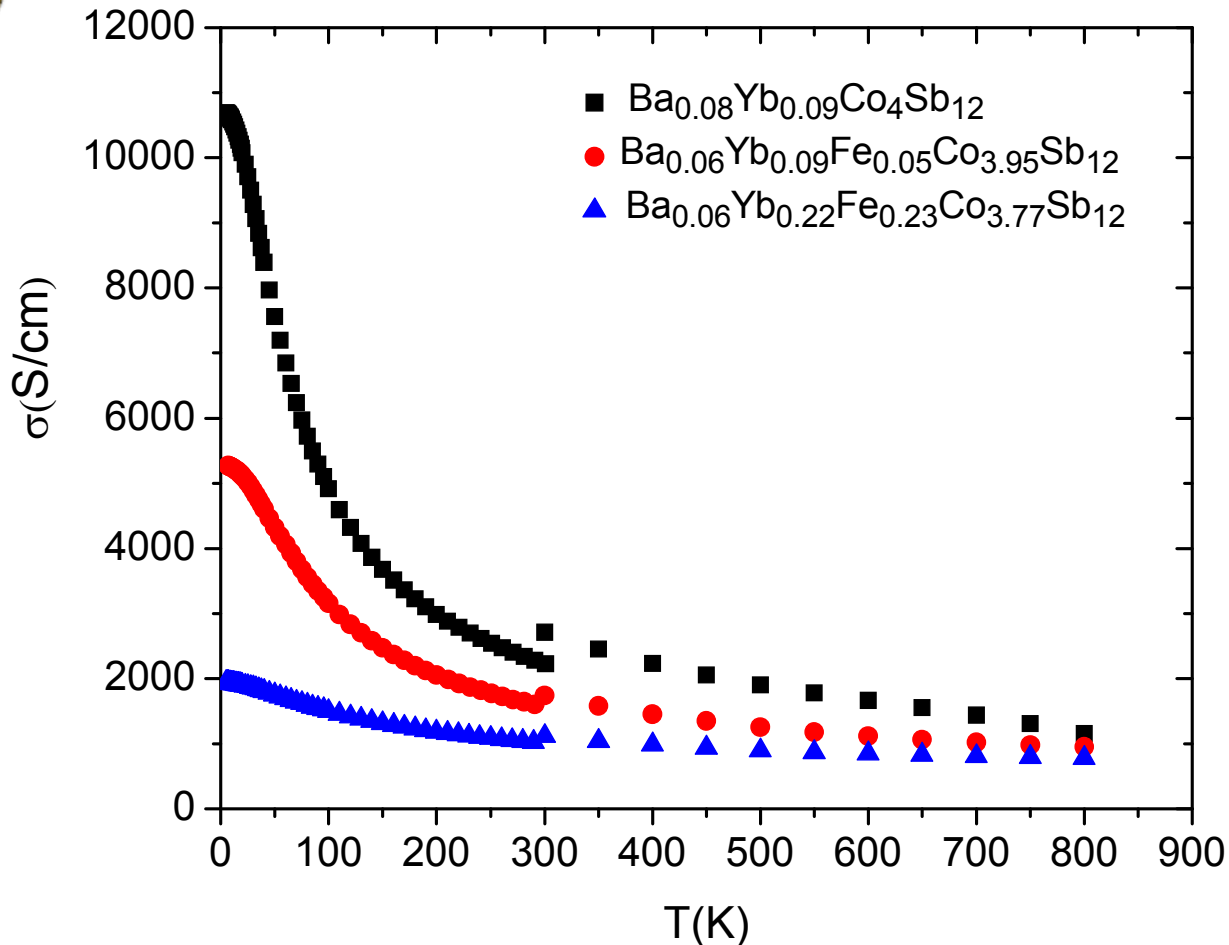
$$n = \frac{A}{eR_H}, \quad A = 1$$



Magnitude indicates a degenerate semiconducting system.
T-dependence suggests excitation of electrons from impurity states.



Electrical conductivity



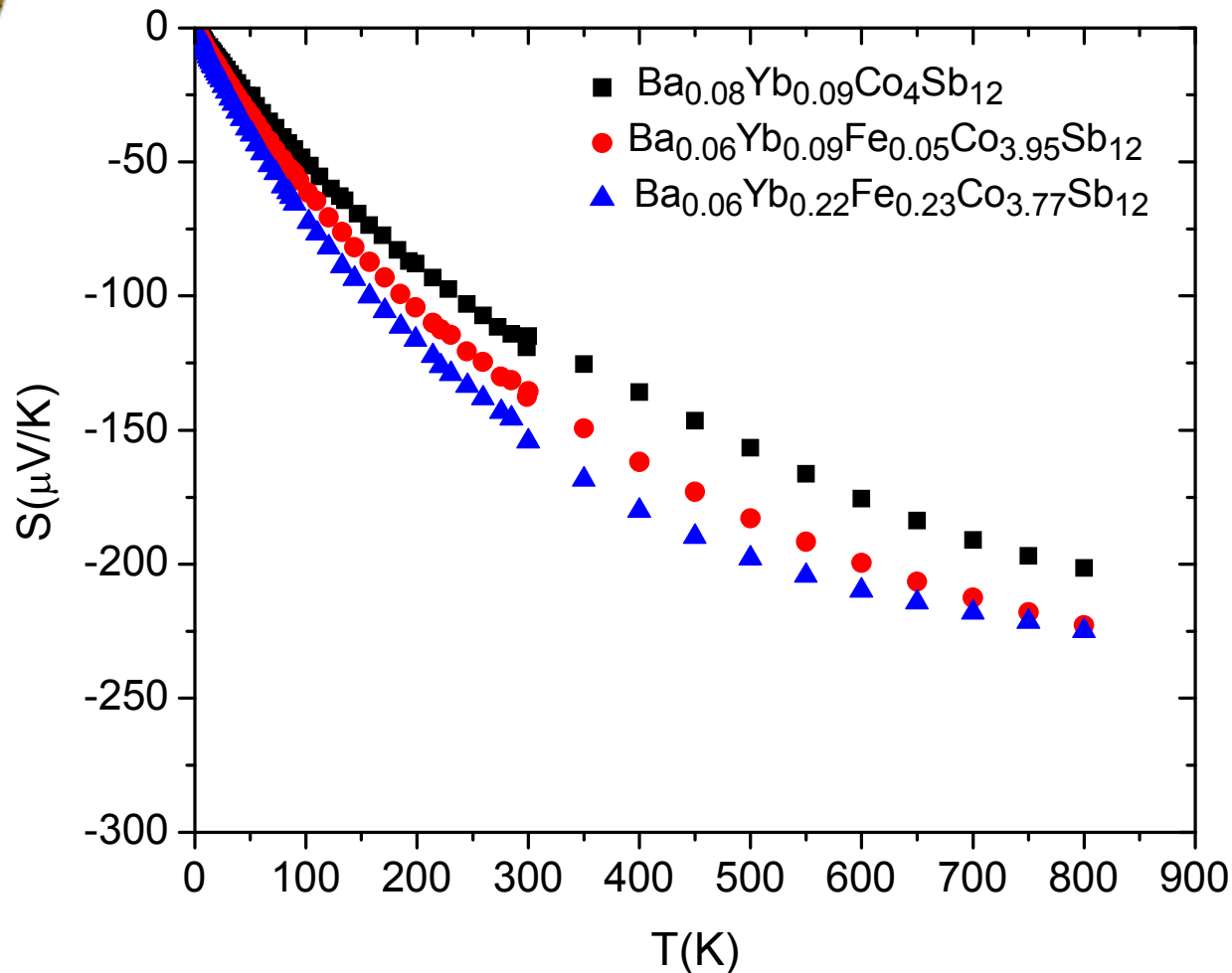
Metallic temperature dependence throughout.

The presence of Fe diminishes conductivity especially at low T.

High-T conductivity on the order of 1000 S/cm.



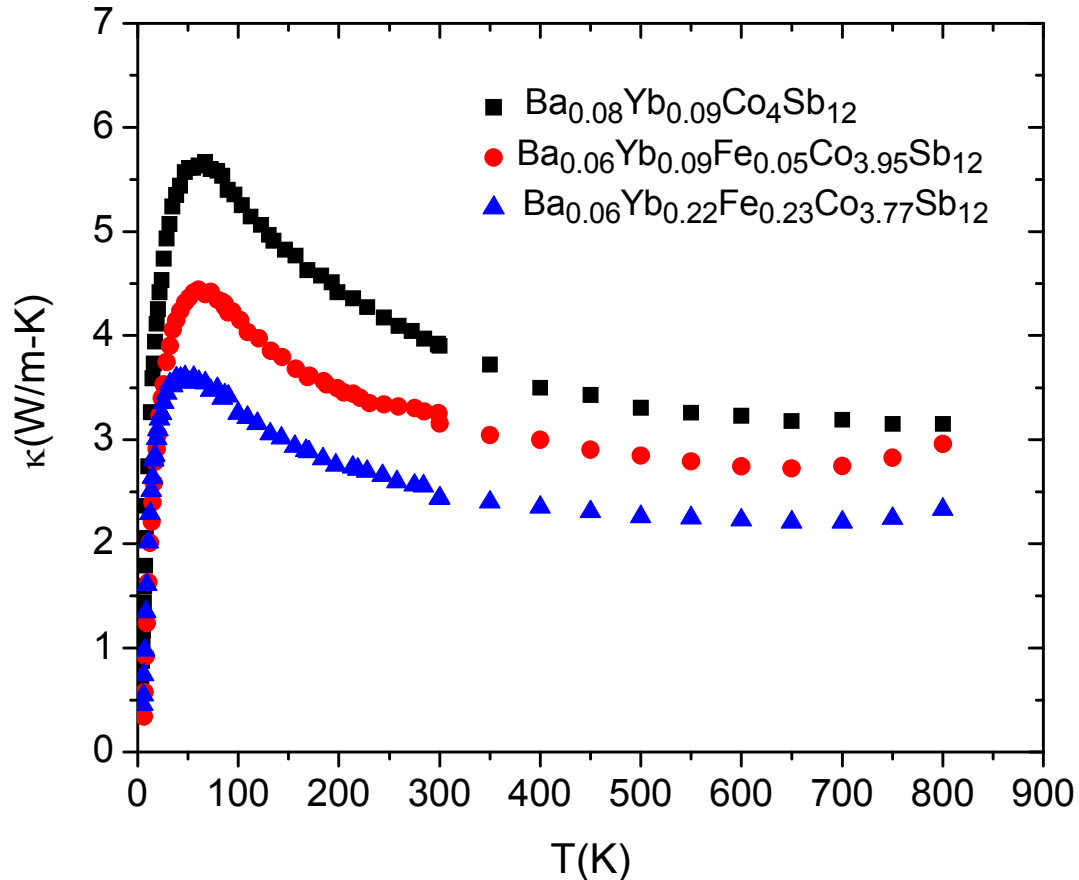
Seebeck coefficient



A monotonous increase in magnitude with temperature.
The presence of Fe actually appears beneficial!
Values on the order of $-225\mu\text{V/K}$ at 800K.



Thermal conductivity



The shape of the data suggests a crystalline behavior.

Thermal conductivity suppressed with increasing content of Fe.

Assuming W-F law, lattice thermal conductivities at 300K are:

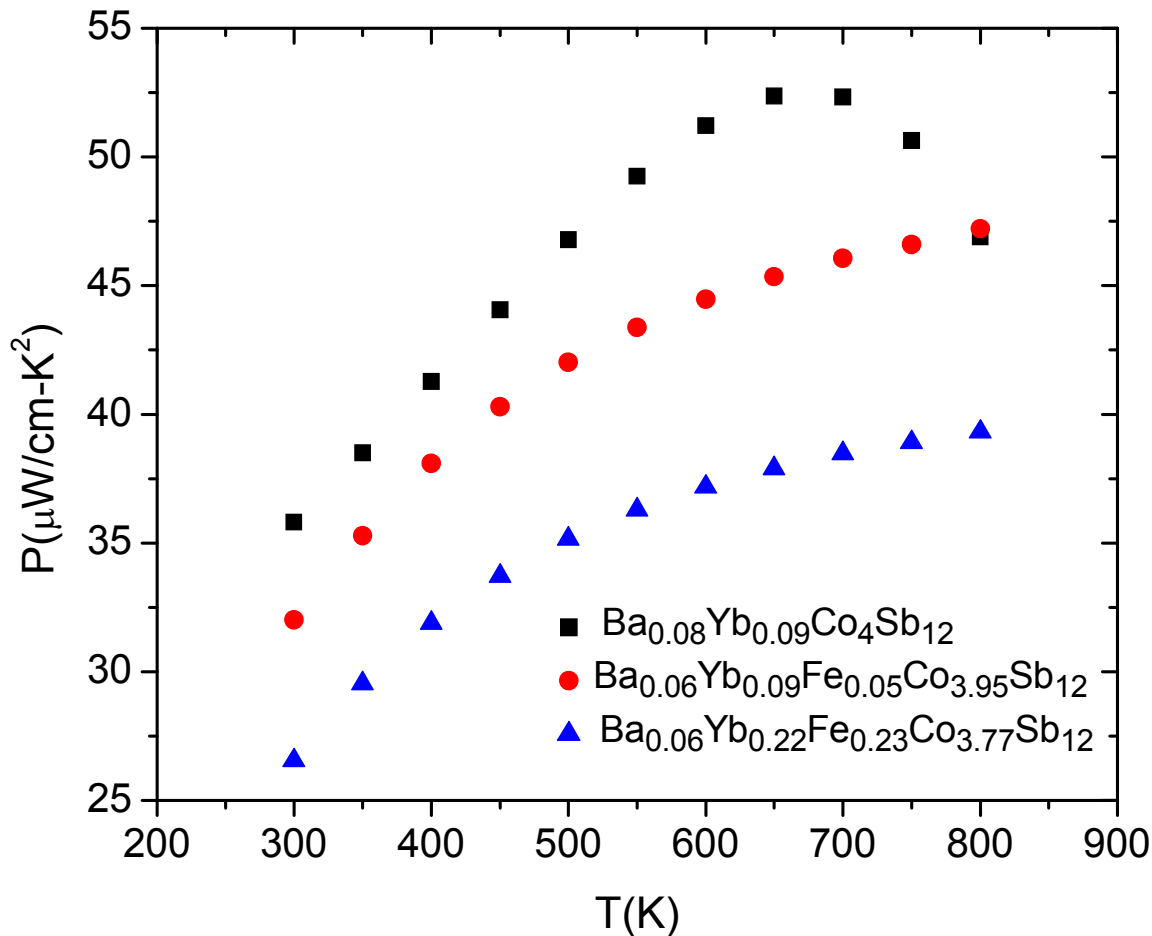
$\text{Ba}_{0.08}\text{Yb}_{0.09}\text{Co}_4\text{Sb}_{12}$
1.95 W/m-K

$\text{Ba}_{0.06}\text{Yb}_{0.09}\text{Co}_{3.95}\text{Fe}_{0.05}\text{Sb}_{12}$
1.8 W/m-K

$\text{Ba}_{0.06}\text{Yb}_{0.22}\text{Co}_{3.77}\text{Fe}_{0.23}\text{Sb}_{12}$
1.6 W/m-K



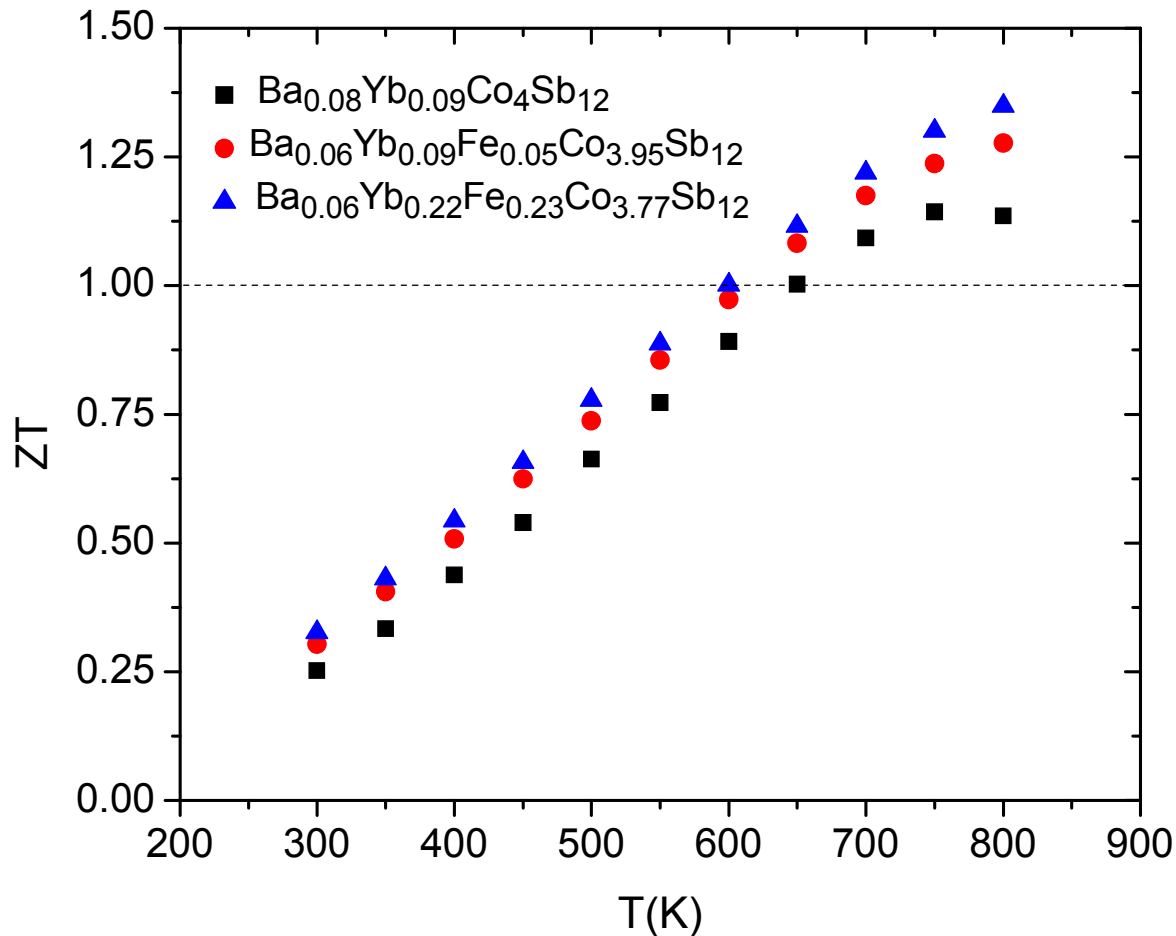
Power factor $P = S^2\sigma$




Electronic properties are adversely influenced by Fe.
Nevertheless, power factors are still quite high.
The control sample (no Fe) enters intrinsic regime above 700K.
Samples containing Fe are still extrinsic at 800K.



Dimensionless figure of merit



Higher Seebeck and lower thermal conductivity with increasing Fe content weigh over the decrease in electrical conductivity  enhanced ZT! ZT values of 1.28 and 1.35 at 800K achieved for Fe-compensated samples. Therefore, another avenue how to reach high ZT on n-type skutterudites.



Conclusions

- Synthesized n-type filled skutterudites partially compensated by Fe.
- Structures support a robust Seebeck coefficient.
- Thermal conductivity is significantly reduced.
- Figures of merit in excess of 1.3 can be achieved using this route.
- More work needed to establish the optimal Fe content and filling fraction.
- Much progress made in developing excellent n-type skutterudites.
- Effort needed to make comparative improvements in p-type skutterudites!

Coupled with their outstanding mechanical properties,
Salvador et al. (2009)
**filled skutterudites show great promise for
waste heat recovery applications.**