Recent Progress in the Development of N-type Skutterudites

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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

$\text{CoSb}_3$ \( \leftrightarrow \Box_2 \text{Co}_8 \text{Sb}_{24} \leftrightarrow \Box \text{Co}_4 \text{Sb}_{12} \)

Cages can be filled with foreign ions \( \leftrightarrow \) **Filled skutterudites**  

Jeitschko (1977)

**Filler species donate electrons**

$R + \text{CoSb}_3 \rightarrow R^n\text{Co}_4\text{Sb}_{12}$  \( R = \text{actinides} \ n = 4^+ \)

rare earth \( n = 3^+, 2^+ \)

alkaline earth \( n = 2^+ \)

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Graph: Carrier density vs. Filling fraction
Binary skutterudites

Possess some of the highest mobilities of all bulk semiconductors.

Unfortunately, thermal conductivity is far too high ($\kappa \sim 10 \text{ W/m-K for CoSb}_3$ at 300K).

Not suitable as thermoelectrics!
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 $\kappa_L$.
- 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


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 $\hbar\omega(Q)$ and $\hbar Q$ can provide answer. One such technique is High Resolution Time-of-Flight Neutron Scattering. The authors used CeFe$_4$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 RCo$_4$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.
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.


Yang et al. (2007) calculated resonant phonon frequencies for filler ions.

Shi et al. (2008) synthesized double-filled Ba$_x$Yb$_y$Co$_4$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 Ba$_{0.3}$Co$_4$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 In$_x$Ce$_y$Co$_4$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

$$R_yFe_{4-x}Co_xSb_{12} \equiv \left( RFe_4Sb_{12} \right)_{\alpha} \left( \square Co_4Sb_{12} \right)_{1-\alpha}$$

Low thermal conductivity is now readily understood: it is not due to mass fluctuation scattering between Fe and Co but between R and ↑(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:

\[ \text{Ba}_{0.1} \text{Yb}_{0.2} \text{Co}_4 \text{Sb}_{12} \] a reference sample

\[ \text{Ba}_{0.1} \text{Yb}_{0.3} \text{Co}_{3.8} \text{Fe}_{0.2} \text{Sb}_{12} \] partly compensated sample

\[ \text{Ba}_{0.15} \text{Yb}_{0.25} \text{Co}_{3.8} \text{Fe}_{0.2} \text{Sb}_{12} \] partly compensated sample

The presence of Fe:
- expands the FFL and
- lowers thermal conductivity
Peritectic system ⇒ 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.
<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Actual Composition (EPMA)</th>
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<tr>
<td>Ba$<em>{0.1}$Yb$</em>{0.2}$Co$<em>4$Sb$</em>{12}$</td>
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Property measurements

Resistivity and Seebeck coefficient

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<800K) 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 increases the density of electrons decreases.

$R_H(10^{-8} \Omega \text{m/T})$

$T(\text{K})$

$\text{Ba}_{0.06}\text{Yb}_{0.09}\text{Fe}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$

$\text{Ba}_{0.06}\text{Yb}_{0.22}\text{Fe}_{0.23}\text{Co}_{3.77}\text{Sb}_{12}$
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.
The presence of Fe actually appears beneficial!

Values on the order of $-225 \mu V/K$ at 800K.
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
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,**

filled skutterudites show great promise for waste heat recovery applications.

*Salvador et al. (2009)*