Chalcogenides and skutterudites as thermoelectric materials: Structural information and improvement of their thermoelectric properties

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THERMOELECTRIC MATERIALS

Materials that can directly and reversibly **convert heat into electrical energy**. Our main goal is to prepare by direct methods, thermoelectric materials with higher conversion efficiency. The efficiency of a thermoelectric device is related with the **figure of merit** of a specific material, defined as:

$$ZT = \frac{S^2\sigma}{\kappa}T$$

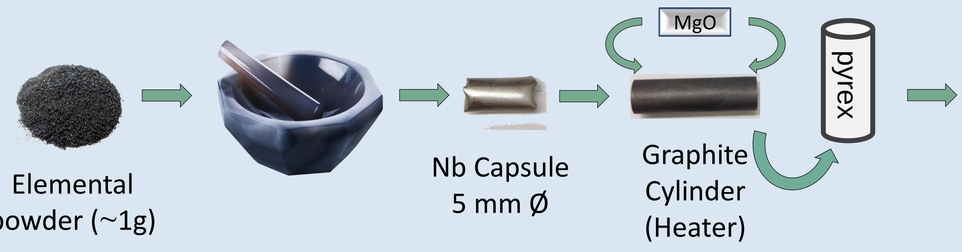
High Seebeck Coefficient (S)
Low Electrical Resistivity (ρ=σ $^{-1}$)
Low Thermal Conductivity (κ)

Commercial materials: $ZT \sim 1$
State-of-the-art materials: $ZT \sim 2-2.5$
Economically competitive devices: $ZT \sim 4$

SYNTHESIS METHODS

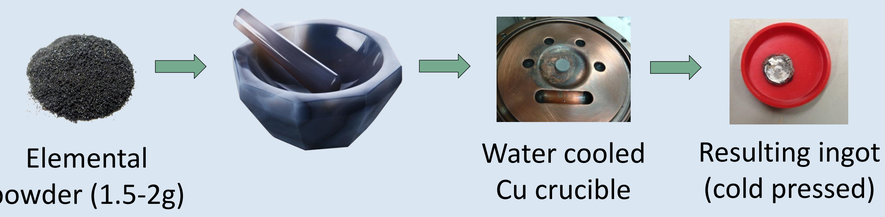
High pressure synthesis → Enhanced kinetics: fast reactions. Stabilizes metastable materials, favors denser phases. We have prepared $R_xCo_4Sb_{12}$ skutterudites.

Named after the city of Skotterud, Norway



2 – 3.5 GPa
800-900 °C
~ 1 h

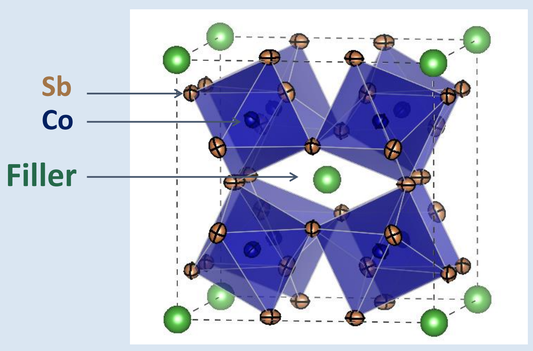
Arc melting synthesis → Short reaction times, and allows the preparation of substantial amounts of sample directly implementable into devices. Highly oriented polycrystalline samples. We have prepared SnSe derivatives.



Up to 3000 °C

~1 min reaction time

SKUTTERUDITES

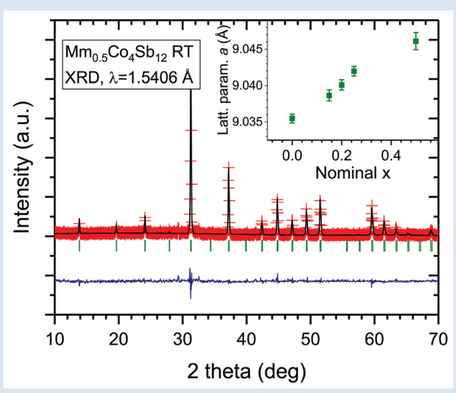


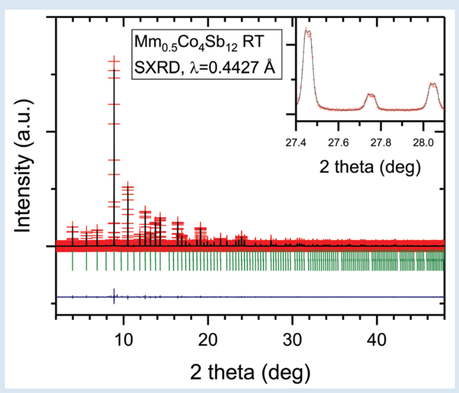
- $CoAs_3$-like cubic structure.
- Lead and telluride free materials.
- High carrier mobility. ✚
- Good Seebeck coefficient. ✚
- High thermal conductivity. ━

Fill the voids in the structure in order to reduce the thermal conductivity

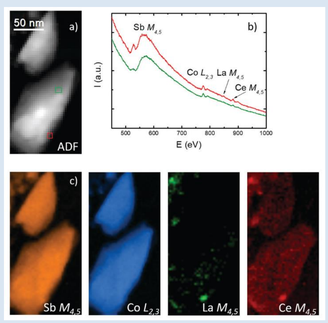
Preparation of nominal: **$R_xCo_4Sb_{12}$ (R = Ce, La, Yb, Sr, K, Mm (Ce+La))**

STRUCTURAL CHARACTERIZATION LABORATORY X-RAYS AND SYNCHROTRON X-RAY DIFFRACTION



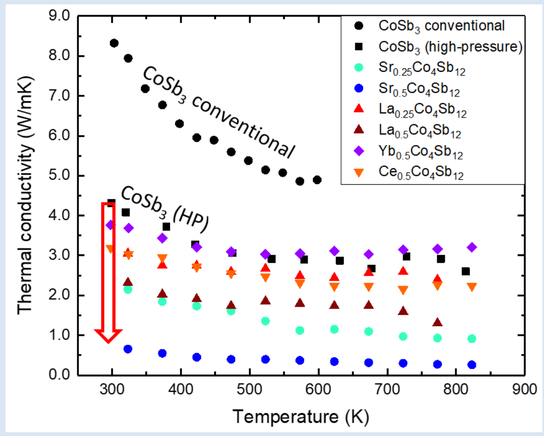


ELEMENTAL MAPPING BASED ON EELS ANALYSIS

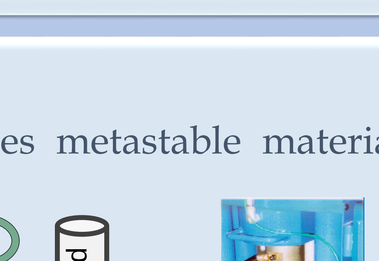


SXRD and EELS confirm the same hypothesis: There is a **phase segregation** in this samples.

THERMAL CONDUCTIVITY MEASUREMENTS



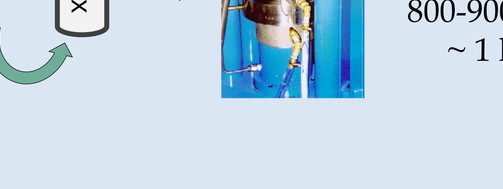
TIN SELENIDE (SnSe) BASED MATERIALS



- Double corrugated layers stacked along the **a** direction.
- Structural phase transition at ~800K.
- High ZT (2.6) reported in single crystals.
- Low thermal conductivity.

$Sn_{0.8}Sb_{0.2}Se$ NEUTRON POWDER DIFFRACTION

SEM IMAGES



This nanostructuration affects the thermoelectric properties.

THERMOELECTRIC PROPERTIES

CONCLUSIONS

- We have successfully prepared **filled skutterudites** using a **high-pressure synthesis** technique.
- The **phase segregation** effect leads to a **reduced thermal conductivity** compared with other skutterudites.
- The arc-melting procedure can produce **nanostructured samples**.
- This nanostructuration affects the thermoelectric properties, for example, **reducing the thermal conductivity** due to **increased scattering of phonons.**

REFERENCES

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3. **Gainza, J.** *et al.* Evidence of nanostructuring and reduced thermal conductivity in n-type Sb alloyed SnSe thermoelectric polycrystals. *J. Appl. Phys.* **126**, 045105 (2019).
4. **Gainza, J**. *et al.* Nanostructured Thermoelectric Chalcogenides. in *Bringing Thermoelectricity into Reality* 3–22 (2018). doi:10.5772/intechopen.75442