Synthesis of nanomaterials by soft chemistry methods for thermoelectric applications

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Introduction

Figure of merit: \[ ZT = \frac{S^2 \sigma}{\kappa} T \]

- S: Seebeck coefficient
- \( \sigma \): electronic conductivity
- \( \kappa \): thermal conductivity

\[ \kappa = \kappa_e + \kappa_l \]

S, \( \sigma \), \( \kappa \) are closely linked properties

⇒ Key issue: to decouple \( S \), \( \sigma \), \( \kappa \)

- ↑ \( \sigma \)
- ↑ \( S \)
- ↓ \( \kappa \)

« Phonon glass - Electron crystal » concept
Strategies to increase ZT:

- Engineering the crystal structure at atomic scale
  - Cage-like materials: skutterudites, clathrates
  - Complex crystals with defaults: half-Heusler compounds, ...
  - Misfits oxides: cobaltites, ...

- Engineering the material structure at the nanoscale
  - Low-dimension materials; nanostructuring
**Contribution of nano-engineering:**

- Dramatic change of the DOS by quantum confinement effect
  - → Increase of $S$

- Semi-metal to semi-conducting transition

- Low-energy carrier filtering at the boundaries
  - → Increase of power factor

- Phonon scattering of phonons at the interfaces
  - → Decrease of $\kappa$
Nanostructured materials:

From theory...

\[ \text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3 \]
Super-lattices
\[ ZT = 2.4 \]

\[ \text{Sb}_2\text{Se}_x\text{Te}_{1-x} \] based quantum dots superlattices
\[ ZT = 1.6 \]

...to experiment.

- Nano_materials
- Nano-composites

M. Dresselhaus, Microscale Thermophysical Engineering, 3 (1999) 100.


Nanostructured materials in devices:

- **Nano-composites**
  - Nano-inclusions: LAST (AgPb$_m$SbTe$_{m+2}$), ...
    - Phase segregation
    - Chemical engineering approach

- **Nano-bulk materials**
  - Super-lattices
    - Costly physical processes
  - Sintered nano-particles
    - Physical/chemical processes

Interest restricted to applications at moderate temperature: mostly Bi$_2$Te$_3$, PbTe, CoSb$_3$
I. Fundamentals of soft-chemistry synthesis
II. Reduction in aqueous medium
III. Reduction in organic solution
IV. Solvothermal synthesis
V. Synthesis in confined medium
VI. Decomposition of organometallic complexes
VII. Post-synthesis treatments

Conclusions/Perspectives
Outline

I. Fundamentals of soft-chemistry synthesis
   1. Generalities
   2. Mechanisms of formation of NPs
   3. Chemical reactions involved in the obtention of NPs

II. Reduction in aqueous medium

III. Reduction in organic solution

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Conclusions/Perspectives
I. Fundamentals / 1. Generalities

2 approaches:

« Top-down »

- volume
- powder
- nanoparticles
- clusters
- atoms

Physical methods:
- Ball milling
- Lithography
- Laser ablation
- Electroexplosion of a wire
- ...

« Bottom-up »

Chemical methods:
- CVD
- Solution chemistry
Advantages and drawbacks of soft-chemistry synthesis

❖ Advantages:

✓ Easy to perform
✓ Often scalable, high yields
✓ Low temperature, low cost
✓ Versatility over crystalline phase, morphology, size
✓ Good control over particle size, distribution, morphology
✓ Good chemical homogeneity, low strain

❖ Drawbacks:

✓ Difficulties to control accurately the stoichiometry
✓ Possible oxide/organic coating of the particles
  → detrimental to densification and electronic properties
I. Fundamentals / 1. Generalities

General procedure for the obtention of nanomaterials

Structure

- XRD
  - Cristallographic phase
  - Impurities
  - Cristallinity
  - Cristallite size
  - Defaults, strains

- TEM
  - HRTEM
  - Electronic diffraction

Stoichiometry

- ICP-AES
- X-ray fluorescence
- EDX
- XPS
- FTIR

Morphology

- SEM
- TEM

Physical

- Electronic properties
- Thermal conductivities
I. Fundamentals / 1. Generalities

General procedure for the obtention of nanomaterials

Characterization $\Rightarrow$ mechanisms of formation

**Intermediate species in solution**
- NMR
- UV-visible spectroscopy

**Intermediate precipitates**
- XRD
- TEM
- ...

**Nucleation/growth**
- SAXS
- UV-visible spectroscopy
- Solution chemical analysis

Centrifugation

sintering

dispersion

coating
1. Induction period

Dissolution of the precursors

1. Induction
2. Nucleation
3. Growth
4. Aging
2. Nucleation

\[ \Delta G(r) = \Delta G_S + \Delta G_{int} \]

\[ \Delta G_S: \text{free enthalpy of the surface} \]

\[ \Delta G_{int}: \text{free enthalpy of formation of the condensed phase} \]

\[ \Delta G(r) = 4\pi r^2 \gamma - \frac{4}{3} \pi r^3 \frac{RT \ln S}{V_m} \]

\[ \gamma: \text{surface tension} \]

\[ S = \frac{c_L}{c_s}; V_m: \text{molar volume} \]

Critical radius:

\[ r_c \Leftrightarrow \frac{d(\Delta G(r))}{dr} = 0 \Leftrightarrow r_c = \frac{2 \gamma}{RT \ln S} \]
3. Growth

2 growth models:

✓ Growth limited by the diffusion of species in solution
✓ Growth limited by the precipitation of monomers
Growth limited by the diffusion of species in solution

\[ J = \frac{4\pi r^2}{V_m} \frac{dr}{dt} \]

The growth rate depends solely of the flux of the monomers supplied to the particles

\[ J = 4\pi r D (C_{bulk} - C_s) \]

Fick law; \( C_s \): concentration at the particle surface
\( D \): diffusion coefficient

\[ \Rightarrow \quad \frac{dr}{dt} = \frac{V_mD}{r} (C_{bulk} - C_s) \]

Growth rate inversely proportional to the radius

\[ \frac{d\sigma^2}{dt} = 2V_mD \left( C_{bulk} - C_s \right) \left[ 1 - \bar{r} \left( \frac{\bar{r}}{r} \right) \right] \]

\[ <0 \]

The variance of the size distribution \( \searrow \) as the particles are growing

\[ \Rightarrow \text{If no additional nucleation growth occurs} \]
\[ \checkmark \text{The smaller the particles are, the faster they grow} \]
\[ \checkmark \text{Focusing effect (dispersion in size} \searrow) \]
I. Fundamentals / 2. Mechanisms of formation of NPs

✓ Growth limited by the precipitation of monomers

Competitive effect: dissolution and precipitation

Growth rate:
\[
\frac{dr^*}{d\tau} = \frac{S - \exp(1/r^*)}{r^* + K \exp(\alpha/r^*)}
\]
with:
\[
r^* = \frac{RT}{2\gamma V_m} r
\]
\[
\alpha: \text{ transfer coefficient}
\]

\[
\tau = \frac{R^2 T^2 D C^0_{seq}}{4\gamma^2 V_m} t
\]

\[
C^0_{seq}: \text{ monomer concentration in solution}
\]

\[
K = \frac{RT}{4\gamma V_m} \frac{D}{4k^0_p}
\]

\[k^0_p: \text{ precipitation rate constant of bulk}\]

K: Damköhler number proportional to diffusion rate/precipitation rate

✓ K low ⇒ diffusion-controlled growth (focusing effect)
✓ K high ⇒ reaction-controlled growth (focusing effect weakened)

4. Aging

2 mechanisms:

- Coalescence

- Ostwald ripening
Strategies to control the particle size

- Seed-mediated growth

\[
C_{080}N_{i20}
\]

homogeneous nucleation

\[
d_m = 1400 \text{ nm}
\]

\[
C_{065}N_{i35}
\]

\[
Pt/CoNi = 2.5 \times 10^{-4}
\]

\[
d_m = 50 \text{ nm}
\]

\[
C_{050}N_{i50}
\]

\[
Pt/CoNi = 0.5 \times 10^{-2}
\]

\[
d_m = 7 \text{ nm}
\]

\[
d_m = \left( \frac{6 \cdot M_{CoNi} \cdot \rho_{germe} \cdot V_{germe}}{\pi \cdot M_{germe} \cdot \rho_{CoNi}} \right)^{\frac{1}{3}} \cdot \left( \frac{[germe]}{[Co + Ni]} \right)^{\frac{1}{2}}
\]

\[
\Rightarrow \text{Control of the size}
\]

Core/shell
I. Fundamentals / 2. Mechanisms of formation of NPs

- **Homogeneous nucleation**
  - Conc. and nature of the reactants, nature of the solvent, reaction time
  - T, P, heating rate, heating mode

Heating rate:
- Co-precipitation
- heating-up
- hot-injection

Heating mode:
- conventional
- Microwave

Used for polar solvent exclusively
- High heating rate
- Uniform heating
- High penetration depth of the wave
- Rapid reaction (a few minutes)
- High yield
- Softer conditions can be used
I. Fundamentals / 2. Mechanisms of formation of NPs

- Homogeneous nucleation
  - Reactivity of the precursors

\[
\text{Ti}^{4+} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2
\]

- Homogeneous nucleation
  - Reactivity of the precursors

- Templatizing strategies
  - Use of a hard/soft template
Strategies to avoid aggregation

Coalescence:

- Templating strategies:
  → Use of a hard/soft template

- Electrostatic stabilization:
  → Modification of the pH, counter-ion...

- Steric stabilization:
  → Addition of polymer, surfactant
  → Use of chelating agents, solvent

- Electro-steric stabilization:
In summary:

Control of nucleation/growth/aging through the synthesis parameters (T, P, time, heating rate and mode, precursor nature, additives, ...)

→ linked to the chemical reactions which depends of the nature of the NPs to synthesize

  a- Oxides
  b- Metals
  c- Chalcogenides
I. Fundamentals / 3. Chemical reactions

a. Synthesis of oxide nanoparticles

→ Sol-gel synthesis
→ Co-precipitation

Sol-gel synthesis

Specific for oxide synthesis
I. Fundamentals / 3. Chemical reactions

**In the presence of water**

**From metal alkoxide precursors**

- **Hydrolysis**
  \[ \equiv M-OR + H_2O \rightarrow \equiv M-OH + ROH \]

- **Condensation**
  \[ \equiv M-OH + HO-M \equiv \rightarrow \equiv M-O-M \equiv + H_2O \]
  \[ \equiv M-OR + HO-M \equiv \rightarrow \equiv M-O-M \equiv + ROH \]

**From metal salts**

- **Dissolution/complexation**
  \[ M^{z+} + N H_2O \rightarrow [M(OH_2)_N]^{z+} \text{ Aquo complex} \]

- **Hydrolysis**
  In basic medium: \[ [M(OH_2)_N]^{z+} + h OH^- \rightarrow [M(OH)_h(OH_2)_{N-h}]^{z+} + hH_2O \]

- **Condensation**
  \[ M-OH + H_2O-M \rightarrow M-OH-M + H_2O \text{ oxolation} \]
  \[ M-OH + HO-M \rightarrow M-O-M + H_2O \text{ oxolation} \]
Example: preparation of cobaltite $\text{Ca}_3\text{Co}_4\text{O}_9$

$i$. Fundamentals / 3. Chemical reactions

$\text{Ca(NO}_3\text{)}_2$
$\text{Co(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}$
water
citric acid

$\text{H}_2\text{O}$

$70^\circ\text{C} - 3\text{h}$
$130^\circ\text{C}, 12\text{h}$

Dried gel

calcination

Calcination $600^\circ\text{C}$, Furnace $900^\circ\text{C}, 8\text{h}$

Calcination $600^\circ\text{C}$, SPS $700^\circ\text{C}, 5\text{min}$

In the absence of water

The oxygen comes from the solvent

**Metal halide in alcohol**

\[
MX_4 + R-OH \rightarrow RX + \equiv M-OH
\]

\[
\equiv M-OH + HO-M \equiv \rightarrow \equiv M-O-M\equiv + H_2O
\]

**Metal halide in ether**

\[
R-OR + MX_4 \rightarrow RX + \equiv M-OR
\]

\[
\equiv M-OR + RO-M\equiv \rightarrow \equiv M-O-M\equiv + ROR
\]
**I. Fundamentals / 3. Chemical reactions**

- **Co-precipitation method in aqueous solution**
  - Oxide preparation

**In aqueous medium**

- aq. NiCl₂
- aq. NH₄OH
- aq. Fe(NO₃)₃
- aq. Ni(NO₃)₂
- aq. Zn(NO₃)₂
- aq. NaOH

**Calcination necessary**

**In organic medium**

- Diethyleneglycol:
  - high boiling T solvent
  - stabilizing agent

**Controlled hydrolysis**
b. Synthesis of metal NPs

❖ Reduction

\[ M^{n+} + ne^- \rightarrow M^0 \quad : \quad E^0_M \]
\[ X^m - ne^- \rightarrow X^{m-n} \quad : \quad E^0_R < E^0_M \]

Usual reductants:

- Borohydride

\[ \text{B(OH)}_4^- + 4\text{H}_2\text{O} + 8e^- \rightarrow \text{BH}_4^- + 8\text{OH}^- \quad E = -1.24\text{V at pH = 14} \]

⇒ Strong reducing agent

- Hydrazine

\[ \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \rightarrow \text{N}_2\text{H}_5^+ + \text{OH}^- \]
\[ \text{N}_2 + 5\text{H}^+ + 4e^- \rightarrow \text{N}_2\text{H}_5^+ (\text{ion hydrazinium}) \quad E^0 = -0.23\text{V} \]

❖ Thermolysis

\[ \text{Co}_2(\text{CO})_8 \rightarrow 2\text{Co} + 8\text{CO} \]
I. Fundamentals / 3. Chemical reactions

c. Synthesis of metal chalcogenide NPs

Example of PbTe and Bi₂Te₃:

❖ Reduction

Precursors:

For PbTe: Pb(+II) and Te(+IV) or Te(0)       For Bi₂Te₃: Bi(+III) and Te(+IV) or Te(0)

\[
\begin{align*}
E^0_{\text{Te}^4+/\text{Te}} &= 0.53 \text{ V} \\
E^0_{\text{Te}/\text{Te}^2^-} &= -1.14 \text{ V} \\
E^0_{\text{Pb}^{2+}/\text{Pb}} &= -0.13 \text{ V} \\
E^0_{\text{Bi}^{3+}/\text{Bi}} &= 0.200 \text{ V}
\end{align*}
\]

2 possible reaction pathways:

\[
\begin{align*}
Pb^{2+} + Te^{2-} &\rightarrow PbTe & 2Bi^{3+} + 3Te^{2-} &\rightarrow Bi_2Te_3 \\
or Pb + Te &\rightarrow PbTe & or 2Bi + 3Te &\rightarrow Bi_2Te_3
\end{align*}
\]

⇒ Reduction of Te and/or Pb/Bi in some cases

⇒ Use of a reductant: often NaBH₄ or N₂H₄
I. Fundamentals / 3. Chemical reactions

- In water/organic solvent
- At ambient pressure/solvothermal conditions
- In confined medium

Soft template: micelles/microemulsions

Hard template
I. Fundamentals / 3. Chemical reactions

- **Thermolysis**

  Bi(III)/Pb(II) complex with ligands:

  \[ \text{Bi(III)/Pb(II)} \] + \[ \text{ligands} \] = \[ M=S C_nH_{2n+1} \] + \[ M=O_2C-C_nH_{2n+1} \]

  Te(-II)-TOP complex in organic solvent

  - Heating-up
  - Microwave
  - Hot-injection
I. Fundamentals of soft-chemistry synthesis

II. Reduction in aqueous medium
   1. Use of organic agents
   2. Templating method

III. Reduction in organic solution

IV. Solvothermal synthesis

V. Synthesis in confined medium

VI. Decomposition of organometallic complexes

VII. Post-synthesis treatments

Conclusions/Perspectives
Advantages/Drawbacks of reduction in aqueous medium

- **Advantages:**
  - Very easy to perform
  - Water = environmental friendly solvent
  - Low cost reactants
  - Absence of organic shells in some cases

- **Drawbacks:**
  - Distribution in size generally high
  - Aggregation difficult to prevent
  - Surface oxidation possible
II. Synthesis in aqueous medium

Strategies to control the morphology and size of the nanoparticles

1. Control of the precursor reactivity and/or particle growth and aggregation:
   - Addition of an organic structuring agent
     - EDTA
       - Ethylenediaminetetraacetic disodium salt
     - \( \text{Bi}^{3+} \) complex
       - Control of the reactivity of ions
       - Control of growth/aggregation
     - Addition of a polymeric agent
       - PVP
       - Polyvinyl pyrrolidone
       - Control of growth/aggregation by steric effect

2. Control of the NPs form and size by sacrificial templating
II. Synthesis in aqueous medium / 1. Use of organic agents

1. Control of the precursor reactivity and/or particle growth and aggregation

- Role of the organic directing agent

**Synthesis of PbTe in the absence of an organic agent**

\[
Pb(CH_3CO_2)_2 \cdot 3H_2O \xrightarrow{H_2O} Aggregated NPs 35 nm-sized \\
Te \text{ aq. KOH} \xrightarrow{} Polydispersity
\]
II. Synthesis in aqueous medium / 1. Use of organic agents

Influence of the nature of the directing agent

1) BiCl₃ + Na₂TeO₃
2) NaBH₄

Preheated H₂O + NaOH + organic agent

24 hours Reflux

Pure Bi₂Te₃

⇒ Importance of the directing agent on the growth and aging of the NPs
⇒ Control over shape and size

II. Synthesis in aqueous medium / 1. Use of organic agents

Influence of the nature of the directing agent

1) $\text{BiCl}_3 + \text{Na}_2\text{TeO}_3$
2) $\text{NaBH}_4$

Preheated $\text{H}_2\text{O}$
+ $\text{NaOH}$
+ organic agent

With EDTA

$\text{Ca}^{2+} \text{H}_{2}\text{Y}^4$ ^

Using $\text{Na}_2\text{TeO}_3$

Nanotubes
d $\approx$ 20-70nm

Using $\text{Te}$

$\approx$ 20 nm-sized particles
congregated into flakes

⇒ Importance also of the precursors on the shape and size

II. Synthesis in aqueous medium / 1. Use of organic agents

Influence of the concentration of the directing agent

\[ \text{Bi(NO}_3\text{)}_3 \text{ in H}_2\text{O} \]

Ascorbic acid

EDTA

\[ + \text{ aq. NaOH} \]

3h

\[ \text{Te aq. NaBH}_4 \]

100°C

\[ \text{Bi}_2\text{Te}_3 \]

\[ [\text{EDTA}] \uparrow \Rightarrow \text{size} \downarrow \]

\[ \text{Bi}_2\text{Te}_3 + \text{Bi}_2\text{TeO}_5 + \text{Te} \]

\[ \Rightarrow \text{Tuning of the reaction product} \]

\[ \Rightarrow \text{Tuning of the size with the directing agent concentration} \]

II. Synthesis in aqueous medium / 1. Use of organic agents

Multiple role of the directing agent

BiCl₃ in aq. HNO₃ + thioglycolic acid

$\text{HS} \quad \text{CO} \quad \text{OH} \quad \rightarrow \quad \text{Bi-SCH}_2\text{CO}_2\text{H}$

complex

H₂O, 70°C

H₂TeO₆ + H₂O

N₂H₄.H₂O

100°C

Bi₂Te₃ nanorods 54 nm


Refluxing time in an aq. thioglycolic acid solution

Incorporation of S ⇒ n-type semi-conductor

⇒ Thioglycolic acid serves as
- directing agent
- doping agent

II. Synthesis in aqueous medium / 2. Templating method

2. Control of the NPs form and size by sacrificial templating

0) NaOH/H₂O
   100°C
1) Na₂TeO₃ + NaBH₄
   1/2h
2) Pb(CH₃CO₂).3H₂O

\[ \text{t}=0 \]
Pure Te

Te nanorods

1) \( \text{TeO}_3^{2-} + \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow \text{Te} + \text{H}_2\text{BO}_3^- + 2\text{OH}^- + 2\text{H}_2 \)

II. Synthesis in aqueous medium / 2. Templating method

2. Control of the NPs form and size by sacrificial templating

0) NaOH/H₂O
100°C
1) Na₂TeO₃ + NaBH₄
1/2h
2) Pb(CH₃CO₂).3H₂O

\[ \text{Pure Te} \]

\[ \text{Te + PbTe} \]

2) \( 3\text{Pb}^{2+} + 2\text{BH}_4^- + 6\text{OH}^- \rightarrow 3\text{Pb} + 2\text{H}_2\text{BO}_3^- + 5\text{H}_2 \)

\( \text{Pb + Te} \rightarrow \text{Pb Te} \)

2. Control of the NPs form and size by sacrificial templating

1) NaOH/H₂O
   100°C
2) Na₂TeO₃+NaBH₄
   1/2h
3) Pb(CH₃CO₂).3H₂O

Nanorods

\[ L = 0.3-2\mu m \]
\[ d = 50-200nm \]

\( t=0 \)
Pure Te

\( t=0 \)
Te + PbTe

\( t=48h \)
Pure PbTe

\( \Rightarrow \) Nanorods constituted of NPS (30-50nm)
\( \Rightarrow \) Absence of organic agents

Outline

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Conclusions/Perspectives
Advantages of organic solvents over water:

✓ Higher boiling temperature
  → Favors crystallinity

✓ Some are chelating agents
  → Control the reactivity of precursors
  → Orientate the form and shape
  → Control the dispersity in size
  → Favors colloidal dispersion

✓ Some are reducing agents
  → Avoid surface oxidation

Drawbacks:

✓ Adsorption of organic species at the particle surface
III. Synthesis in organic medium

### Polyol synthesis

- Polar solvent, high $\varepsilon_r$ and $T_{\text{boiling}}$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_b$ ($^\circ$C)</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>100</td>
<td>78,5</td>
</tr>
<tr>
<td>ethanol</td>
<td>78,5</td>
<td>24</td>
</tr>
<tr>
<td>1,2-ethanediol</td>
<td>198</td>
<td>38</td>
</tr>
<tr>
<td>1,2-butanediol</td>
<td>192</td>
<td>22</td>
</tr>
<tr>
<td>Diethyleneglycol</td>
<td>245</td>
<td>32</td>
</tr>
</tbody>
</table>

Chemical structures:

- Water: \(\text{H}_2\text{O}\)
- Ethanol: \(\text{CH}_3\text{OH}\)
- 1,2-Ethanediol: \(\text{CH}_3\text{CH(OH)OH}\)
- 1,2-Butanediol: \(\text{CH}_3\text{CH(OH)CH(OH)}\)
- Diethyleneglycol: \(\text{OCH}_2\text{CH(OH)OH}\)
III. Synthesis in organic medium

Polyol synthesis

- Polar solvent, high $\varepsilon_r$ and $T_{\text{boiling}}$
- Reducing agent

$\Rightarrow$ Avoid surface oxidation

- Complexing agent

\[
\begin{align*}
\text{Complex metal ions} \\
\text{Adsorption on the particle surface} \\
\Rightarrow \text{Control of nucleation and growth}
\end{align*}
\]
III. Synthesis in organic medium

Optimisation of the reaction parameters: the case of CoSb$_3$

Reaction parameters: T, time, reactant nature, concentration, organic agents...

Influence of temperature

\[
\text{CoCl}_2 + 2\text{NaBH}_4 \rightarrow \text{Co} + 2\text{BH}_3 + 2\text{NaCl} + \text{H}_2 \\
2\text{SbCl}_3 + 6\text{NaBH}_4 \rightarrow 2\text{Sb} + 6\text{BH}_3 + 6\text{NaCl} + 3\text{H}_2 \\
\text{Co} + \text{Sb} \rightarrow \text{CoSb} \ (165^\circ \text{C}) \\
\text{CoSb} + 2\text{Sb} \rightarrow \text{CoSb}_3 \ (T \geq 180^\circ \text{C})
\]

\[\Rightarrow\] Possibility of obtaining CoSb$_3$ pure and well crystallized with the adequate parameters

III. Synthesis in organic medium

Optimisation of the reaction parameters: the case of CoSb$_3$

---

Influence of time

CoSb$_2$ and traces of Co appear with prolonged time

CoSb$_3$ → CoSb$_2$ +Co

⇒ CoSb$_3$ is metastable (idem ball milling)

⇒ Possibility of obtaining CoSb$_3$ pure with the adequate parameters

---

III. Synthesis in organic medium

Synthesis of solid solutions: the case of Bi$_2$(Te,Se)$_3$

Different precursors in solution

\[ \text{Bi(NO}_3\text{)}_3 \cdot \text{H}_2\text{O} \]
\[ \text{K}_2\text{TeO}_3 \cdot \text{H}_2\text{O} \]
\[ \text{Na}_2\text{SeO}_3 \]

240°C, 4/5h

\[
\begin{align*}
\text{Bi}_2\text{Te}_3 \\
\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3} \\
\text{Bi}_2\text{Se}_3
\end{align*}
\]

Nanoplates

\[ \Rightarrow \text{Control over stoechiometry} \]

Te/Se ratio \[ \uparrow \]

SPS 250°C, 40MPa

Orientation of the NPs after pelletization

\[ \Rightarrow \text{Formation of solid solution with controlled stoichiometry} \]

I. Fundamentals of soft-chemistry synthesis

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III. Reduction in organic solution

IV. Solvothermal synthesis
   1. Control of the stoichiometry
   2. Control of the morphology
   3. Nanoplating

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Conclusions/Perspectives
**IV. Solvothermal synthesis**

**Solvothermal conditions**

\[ T > T_B \text{ in an autoclave } \Rightarrow P > P_{\text{atm}}. \]

Idea: to reproduce the geological conditions

Modification of the solvent properties

\[ \Rightarrow \text{modification of chemical reactions} \]

\[ \Rightarrow \exists \text{ of } \varepsilon \text{ and } \eta \]

\[ \Rightarrow \text{higher mobility of dissolved species} \]

\[ \Rightarrow \text{lower polarity} \]

\[ \Rightarrow \text{Equilibrium constants modified (}K_e \uparrow, \ldots)\]
IV. Solvothermal synthesis

Advantages of solvothermal conditions over ambiant pressure

✓ Versatile method (over cristalline phase, morphology, size)
✓ High cristallinity
✓ Good chemical homogeneity
✓ Excellent control over morphology and particle size distribution

Same principle as ambiant pressure synthesis:

1. Control of the stoichiometry
   → optimization of the synthesis conditions

2. Control of the morphology
   → use of organic agents
   → sacrificial templating

3. Obtention of nanocomposites by nanoplating
1. Control of the stoichiometry

Optimisation of the synthesis conditions: solvothermal synthesis of CoSb$_3$

Phase segregation in the case of CoSb$_3$?

\[
\text{Sb} + \text{CoSb}_2 \rightarrow \text{CoSb}_3
\]

CoCl$_2$·6H$_2$O
SbCl$_3$
NaBH$_4$
TriEG
290°C

12h: CoSb$_3$
3 h: CoSb$_3$, Sb, CoSb$_2$
1 h: CoSb$_3$, Sb, CoSb$_2$
RT

⇒ Possibility of obtaining CoSb$_3$ pure with the adequate parameters

IV. Solvothermal synthesis / 1. Control of the stoichiometry

Obtention of solid solution: the case of $\text{CoSb}_{3-x}\text{Fe}_x$

NPs size: 10nm

(a) $X = 0$

(b) $X = 0.5$

(c) $X = 0.8$

(d) $X = 1.0$

NPs size: 20nm

Evolution of the cell parameter with [Fe]

$\text{FeCl}_3.6\text{H}_2\text{O}$

$\text{CoCl}_2.6\text{H}_2\text{O}$

$\text{SbCl}_3$

$\text{NaBH}_4$

$\text{TriEG}$

$290^\circ\text{C}$

$\Rightarrow$ Vegard law

$\Rightarrow$ Possibility of controlling the stoichiometry of solid solution

2. Control of the morphology

Use of organic agents: the case of Bi$_2$Te$_3$ flower-like nanocrystals

$\Rightarrow$ Very well crystallized Bi$_2$Te$_3$ flower-like nanocrystals

Growth direction: (11$ar{2}$0)

Top-bottom facets: (0001); side facets (11$ar{2}$0)

$\Rightarrow$ Control of the direction growth

IV. Solvothermal synthesis / 2. Control of the morphology

- **Role of PVP:**
  - without
  - with

  \[ \Rightarrow \text{PVP: stabilizing agent} \]

- **Role of acetic acid:**

  \[ \Rightarrow \text{Acetic acid: structure directing agent} \]

- **Self-assembly organisation:**
  - 2D-film
  - Honey-comb like spheres

Templating strategy

Example of the synthesis of PbTe from Te nanorods

\[ \text{Pb(NO}_3\text{)}_2 \rightarrow \text{NaOH} \]

Te nanorods

160°C, 6h

Topotactic transformation

⇒ Sacrificial templating strategy to control the form and size

3. Obtention of nanocomposites by nanoplating

Bulk CoSb₃

CoCl₂
SbCl₃

Absolute ethanol
Ethylenediamine
NaBH₄

240°C, 80h

NPs precipitates on the bulk CoSb₃ surface

⇒ Formation of nanocomposites

Hot pressing
N₂, 500°C, 30 min.

Nanostructuring retained after densification

⇒ Nanostructuring lowers the thermal conductivity
I. Fundamentals of soft-chemistry synthesis

II. Reduction in aqueous medium

III. Reduction in organic solution

IV. Solvothermal synthesis

V. Synthesis in confined medium
   1. Use of reverse micelles
   2. Use of non stabilized biphasic medium

VI. Decomposition of organometallic complexes

VII. Post-synthesis treatments

Conclusions/Perspectives
V. Synthesis in confined medium / 1. Reverse micelles

1. Use of reverse micelles as nano-reactors

Principle

→ Stable emulsions

Reaction inside the nano-reactor by content exchange

Merged micelles during a few nanoseconds

⇒ Content exchange
⇒ Reaction
V. Synthesis in confined medium / 1. Reverse micelles

- **Modulation of the size of reverse micelles**

  \[ w = \frac{[H_2O]}{[AOT]} \]

  ![Diagram of reverse micelles](image)

- **Modulation of the form of the reverse micelle**

  ![Images of reverse micelles](image)

- **Advantages:**
  - Particle size in the nanometer range
  - Modulation of the size of the NPs to some extent
  - Modulation of the form of the NPS
  - Possibility of obtaining solid solutions
    - Use of a ligand as dopant
    - Use of multiple micellar solutions

- **Drawbacks:**
  - Difficult to scale up

Example of Co NPS

Use of a ligand as a dopant

$L=$ thioglycolic acid

After annealing: $\text{Bi}_2\text{Te}_3 + \text{Bi}_2\text{Te}_2\text{S}$

$\Rightarrow$ Incorporation of $S$ from thioglycolic acid
$\Rightarrow$ Protection against oxidation

Micelles of dioctyl sodium sulfosuccinate (AOT) in isooctane

$\omega=2.4$  $\Rightarrow$ Well crystallized NP
$\Rightarrow$ Non agglomerated NPs
$\Rightarrow$ Size ↑ with $\omega$ (2.5 to 10.4 nm)

$\omega=4.1$

Use of multiple micellar solutions

Reverse micelles of SDS in octane + 1-butanol

1) Micellar solution containing Ag(NO₃)
+ micellar solution containing K₂Sb(C₄H₂O₆)₂
+ micellar solution containing Pb(NO₃)₂
2) Addition of a micellar solution containing Na₂TeO₃/K₂Te
3) Addition of a micellar solution containing NaBH₄

AgPb₂SbTe₄
AgPbSbTe₃
AgSbTe₂

⇒ Formation of pure LAST alloys

⇒ High atomic order

⇒ Nanometric size
⇒ Well dispersed NPs
⇒ Size dispersity

2. Use of non-stabilized biphasic medium

\[ \text{BiCl}_3 \quad \text{TeCl}_4 \quad \text{EG} \quad \text{C}_{12}\text{H}_{25}\text{SH} \]

\[ \text{Bi}^{3+} \quad \text{Te}^{4+} \]

EDX

2. Use of non-stabilized biphasic medium

$\text{BiCl}_3\quad \text{TeCl}_4\quad \text{EG}\quad \text{C}_{12}\text{H}_{25}\text{SH}$

$\text{HO-CH}_2-\text{OH}$

$\text{Bi}^{3+}$

$\text{Te}^{4+}$

$\Rightarrow$ Hollow spheres
V. Synthesis in confined medium / 2. Emulsions

2. Use of non-stabilized biphasic medium

\[
\text{BiCl}_3 + \text{TeCl}_4 + \text{EG} + \text{C}_{12}\text{H}_{25}\text{SH} \rightarrow \text{Hollow spheres constitutted of monocristaline platelets of Bi}_2\text{Te}_3
\]

⇒ Hollow spheres constituted of monocristaline platelets of Bi\textsubscript{2}Te\textsubscript{3}

⇒ Aligned platelets

Outline

I. Fundamentals of soft-chemistry synthesis

II. Reduction in aqueous medium

III. Reduction in organic solution

IV. Solvothermal synthesis

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VI. Decomposition of organometallic complexes
   1. Synthesis of simple chalcogenides
   2. Synthesis of solid solutions
   3. Synthesis of hetero-nanostructures

VII. Post-synthesis treatments

Conclusions/Perspectives
Decomposition of organometallic complexes

Example of $\text{Bi}_2\text{Te}_3$

Bi(III) complex

Te(-II) complex

Ligand:
$C_n\text{H}_{2n+1}\text{SH}$
$C_n\text{H}_{2n+1}\text{CO}_2\text{H}$

Inert atmosphere
$T \approx 150 - 200^\circ C$

- Advantages:
  - Very small nanoparticles ($d < 10\text{nm}$) in the case of hot injection
  - Monodispersity in size and form
  - Possibility of tuning the size and form
  - Colloidal solutions (very well dispersed capped particles) or films

- Drawbacks:
  - Presence of an organic shell
1. Synthesis of simple chalcogenides

Synthesis of Bi$_2$Te$_3$ from Bi-thiol complexes

Importance of the formation of the Bi-thiol complex:

Without thiol

With C$_{12}$H$_{25}$SH at 150°C

⇒ Particle morphology, size, dispersity control
Influence of the capping agent chain length:

Alkanethiol chain length $\uparrow$

The alkanethiol remains adsorbed at the NPs surface

Steric protection of the newly formed particles $\Rightarrow$ inhibition of particle growth

Influence of the temperature:

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>50°C</th>
<th>150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_8H_{17}SH$</td>
<td>29±5</td>
<td>98±15</td>
</tr>
<tr>
<td>$C_{12}H_{25}SH$</td>
<td>23±3</td>
<td>45±6</td>
</tr>
<tr>
<td>$C_{18}H_{37}SH$</td>
<td>17±2</td>
<td>52±7</td>
</tr>
</tbody>
</table>

High temperatures favors growth $\Rightarrow$ Possibility of tuning the particle size

M.R. Dyrmier, Small. 5 (2090) 933.
Influence of the temperature:

- \( T < 170 \^\circ C \):
  - Monodisperse cubic-octahedral NPS

- \( T > 200 \^\circ C \):
  - Less monodisperse cubic NPS
  - Larger size

⇒ High temperature favors growth
⇒ Change of shape with size (Wulff construction)

---

Influence of the oleic acid/Pb acetate ratio

Oleic acid/Pb acetate molar ratio

The size with the addition of oleic acid

Stability of lead oleate > lead acetate
→ Lead oleate reacts more slowly
→ Less nuclei

⇒ Possibility of tuning the particle size with the ligand

Deposition of QDs lattices

Tape casting of a PbTe colloidal solution

⇒ High degree of orders; interesting structures for thermoelectricity

---

VI. Decomposition of complexes / 2. Solid solutions

2. Synthesis of solid solutions

Doping of PbTe by iodine

⇒ Pure I doped-PbTe nanoparticles (4-5% depending on the initial ratio) with tunable size
⇒ n-type semi-conductors (non-doped PbTe is p-type)
⇒ $S^2\sigma \searrow$ with I doping for a same size

VI. Decomposition of complexes / 2. Solid solutions

Synthesis of quaternary nanocrystals

1) Pb(II)oleate
Sb(II) oleate
octadecene
2) Ag-dodecanethiol complex

Te(-II)-TOP complex

N₂, 150 °C, 2 min

Pure LAST solid phase

AgPbₐSbTeₐ+2

⇒ Formation of a pure solid solution of AgPbₐSbTeₐ+2 (m=1-18)

Morphology of the NPs

\[ \text{AgPb}_m\text{SbTe}_{m+2} \]

- \( m_{\text{th}} = 2 \)
  - \( m_{\exp} = 2.44 \)
- \( m_{\text{th}} = 4 \)
  - \( m_{\exp} = 3.96 \)
- \( m_{\text{th}} = 6 \)
  - \( m_{\exp} = 7.69 \)
- \( m_{\text{th}} = 8 \)
  - \( m_{\exp} = 9.87 \)
- \( m_{\text{th}} = 18 \)
  - \( m_{\exp} = 25.7 \)

⇒ Well crystallized
⇒ Highly monodisperse NPs
⇒ Diameter = 6.8-8.4nm

Effect of annealing

At 150°C, crystallite size ↑ from 6.3 to 14.5 nm

Phase separation upon annealing at 150°C within the nanocrystals but no morphological changes observed

VI. Decomposition of complexes / 3. Hetero-nanostructures

3. Preparation of hetero-nanostructures

Pb/oleate complex
In diphenylether

Te(-II)-TOP complex

Se(-II)-TOP complex

+ Pb/oleate complex in diphenylether

PbTe NPs

PbTe-PbSe core-shell nanostars

Epitaxial growth of PbSe in the [100] direction onto each of 6 the octahedron tips

M. Scheele, ACS Nano 5 (201) 8541.
4. Preparation of composite films

Binary QDs lattice

PbTe + AgTe colloidal solutions followed by self-organization evaporation

⇒ High degree of orders
⇒ Structure depending upon the NPs size

⇒ Modulation of $\sigma$

Measures after $\text{N}_2\text{H}_4$ treatment (see after)

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   3. Synthesis of hetero-nanostructures
VII. Post-synthesis treatments
   1. Thermal treatments
   2. Chemical treatments

Conclusions/Perspectives
Possible organic/oxide coating: drawback of the solution synthesis

→ detrimental to densification and electronic properties

Is it a fatality?

1. Thermal solutions (annealing)
2. Chemical solutions
VII. Post-synthesis treatments / 1. Thermal treatments

1. Thermal treatments

- Annealing under N₂ flow

<table>
<thead>
<tr>
<th>Use of C₁₈H₁₇SH</th>
<th>Particle size (nm)</th>
<th>σ (S cm⁻¹)</th>
<th>S (μV K⁻¹)</th>
<th>S²σ (μV²cm⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Bi₂Te₃</td>
<td></td>
<td>12.2</td>
<td>-125</td>
<td>1.9 10⁵</td>
</tr>
<tr>
<td>NPs synthesized</td>
<td>52±7</td>
<td>5.89 10⁻¹</td>
<td>-85</td>
<td>2.5 10³</td>
</tr>
<tr>
<td>at T = 50°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

⇒ Poor electronic properties

NPs obtained by decomposition of organometallic complexes (Bi-SCₙH₂ₙ₊₁ and Te-TOP)

⇒ Nanostructuration retained

thermal treatment: 350°C, 24h, under N₂ flow

densification, $d \approx 87\%$ after cold compaction

<table>
<thead>
<tr>
<th>Use of $\text{C}<em>{18}\text{H}</em>{17}\text{SH}$</th>
<th>Particle size (nm)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$S$ ($\mu$V K$^{-1}$)</th>
<th>$S^2\sigma$ ($\mu$W cm$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPs before annealing</td>
<td>17±2</td>
<td>1.07 $10^{-3}$</td>
<td>-49</td>
<td>2.6 $10^{-6}$</td>
</tr>
<tr>
<td>NPs after annealing</td>
<td>39±7</td>
<td>30.4</td>
<td>-150</td>
<td>0.69</td>
</tr>
</tbody>
</table>

$\Rightarrow$ Improvement of the power factor due to
- removal of the organic shell
- sulfur doping during annealing

Absence of T dependence different from bulk $\text{Bi}_2\text{Te}_3$

at 300 K: $\kappa(\text{NPs}) = 0.51 \text{ W m}^{-1}\text{K}^{-1} \ll \kappa(\text{bulk})$
VII. Post-synthesis treatments / 1. Thermal treatments

Advantages of thermal treatment under N\textsubscript{2} flow:

✓ Removal of the organic surface layer $\Rightarrow$ electronic properties
✓ Keeping nanostructuration layer $\Rightarrow$ low $\kappa$

Drawbacks:

😊 Small increase of oxide content

$\Rightarrow$ Thermal treatment under N\textsubscript{2} flow do not permit to remove the oxide layer

\textit{M.R. Dyrmier, Small. 5 (2009) 933.}
Annealing under Ar flow

NPs obtained by decomposition of Bi-thiol (C\textsubscript{12}H\textsubscript{25}SH) and Te-TOP complexes

Annealing for 5 hours under Ar flow

Cold-pressing

⇒ No oxide formation

Bi\textsubscript{2}Te\textsubscript{3}

Vacuum-dried

T = 300°C

T = 350°C

T = 380°C

⇒ Nanostructured materials up to 350°C
VII. Post-synthesis treatments / 1. Thermal treatments

\( \text{Bi}_2\text{Te}_3 \)

- ✓ Low \( \sigma \) before annealing
- ✓ \( \sigma \) \( \uparrow \) with annealing \( T \)
- ✓ n-type semi-conductor
- ✓ \( S \) max for \( T=300\,^\circ \text{C} \)

\( \Rightarrow \) Simultaneous \( \uparrow \) of \( \sigma \) and \( S \) at annealing \( T \) of 300\,^\circ \text{C}

Data non-corrected from radiation loss

- ✓ Weak \( \uparrow \) of \( \kappa_L \) with \( T \) due to phonon scattering through nanostructuring
- ✓ Low \( \kappa_L \) values which increases with annealing

\( \Rightarrow \) Ar flow annealing permits to remove the capping ligand without oxidation

VII. Post-synthesis treatments / 2. Chemical treatments

2. Chemical treatments

- Acidic treatment to remove the oxide shell:

  Bi$_2$Te$_3$ prepared by ball milling treated in a 5%wt HCl solution

  ⇒ Removal of the oxide layer

  Composites of Bi$_2$Te$_3$ in PEDOT:PSS

  ⇒ Both $\sigma$ and $S$ increase

Chemical exchange to remove organic ligands:

1) Exchange of dodecanethiol ligand shell by oleic acid on the surface of nanoparticles obtained by complexes decomposition

2) Hydrazine (or ammoniac) etching treatment

- Base which can remove the capping agent
- Reducing agent

3) SPS treatment (50°C)

<table>
<thead>
<tr>
<th>sample</th>
<th>Resistivity (mΩ cm)</th>
<th>S (μV K⁻¹) (300K)</th>
<th>κ (W m⁻¹ K⁻¹) (200K)</th>
<th>zT (300K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type bulk Bi₂Te₃</td>
<td>1.4</td>
<td>-180</td>
<td>2.2</td>
<td>0.32</td>
</tr>
<tr>
<td>this work</td>
<td>1.3</td>
<td>-80</td>
<td>0.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

⇒ Same resistivity as bulk n-Bi₂Te₃
⇒ Lower thermal conductivity.

N$_2$H$_4$ treatment of a PbTe film followed by thermal treatment

⇒ Interparticle distance ↓ from 1.8 down to 0.3 nm
⇒ Quantum dots nature preserved with:
- hydrazine treatment
- thermal treatment up to 200°C (vacuum)

⇒ Same resistivity as bulk n-Bi$_2$Te$_3$
⇒ Lower thermal conductivity.

VII. Post-synthesis treatments / 2. Chemical treatments

- Molecular Metal Chalcogenide complexes (MMC)
  - Use as capping agents

Formation of MMC:
- dissolution in hydrazine of bulk metal chalcogenides in the presence of an excess of chalcogenide

MMC/N₂H₄ → N₂H₄ + MMC-capped NPs

PbSe obtained by decomposition of complexes (insets) and after MMC treatment (main TEM images)

⇒ Same crystalline structure
⇒ Inter-particle distance \( \downarrow \) from 1.4 to <0.3 nm


VII. Post-synthesis treatments-2. Chemical treatments

Electronic properties:

- $\sigma \times 10^8$ after MMC treatment
- $\sigma = 110-320 \text{ S cm}^{-1} \text{ at } 300\text{K}$
- $\sigma \uparrow$ with NPs size
- $\sigma \uparrow$ with $T$ (low energy carrier filtering)

Thermal properties:

- n-type (due to MMC)
- $S \uparrow$ when NPs size $\downarrow$ (quantum confinement)
- $S \uparrow$ at high $T$ (release of low energy carriers and $\uparrow$ of minority hole carriers)
- low $\kappa$
- $\kappa \uparrow$ with NPs size ($\downarrow$ interface density)

Thermoelectric properties:

- High $ZT$
VII. Post-synthesis treatments / 2. Chemical treatments

Post-synthesis colloidal atomic layer deposition

Removal of the capping agent and engineering stepwise the surface stoichiometry

Oleic acid capped PbSe NCs

Spin casting

Connection along the (100) facets first (due to weaker bound oleic ligand)

After 1 cycle

After 2-3 cycles

⇒ Post-synthesis charge carrier control

⇒ High electron mobility: 4.5 cm²/(V.s)
Advantages of soft-chemistry synthesis:

- Variety of chemical routes and strategies to control:
  - the crystalline phase
  - the stoichiometry
  - the morphology
  - the particle size, dispersity
- Scalable, high yields, low temperature, low cost
- Good chemical homogeneity, high crystallinity, low strain
- Possibility of designing a high variety of simple or complex materials:
  - simple chalcogenides (PbTe, Bi$_2$Te$_3$, CoSb$_3$)
  - solid solutions ((Bi,Sb)$_2$Te$_3$, Bi(Te,Se)$_3$, Co (Sb,Fe)$_3$, AgPb$_m$SbTe$_{2+m}$)
  - core-shell NPs
  - nanocomposites
- Obtention of dense and non oxidized materials through post-treatments
Conclusions/Perspectives

Improvement ways:

- From « essay-error » to a reasonned approach
- Pursuit of efforts to design in a same material both:
  - nanostructuring
  - chemical stoichiometry (solid solution)

⇒ optimization of $\sigma$, $S$ and $\kappa$ in the same material

Towards advanced materials:

Pt nanocubes encapsulated in Sb$_2$Te$_3$


⇒ S improved due to filtering of low energy holes
⇒ but decrease of $\sigma$ due to mobility reduction
⇒ Slightly improved power factor
Thank you for your attention
Some questions?
Te/Se-\((C_8H_{17})_3P\) complex \(\rightarrow\) Quick, efficient and scaling up synthesis

Bi/Sb-\(S(CH_2CO_2H)\) complex

Thioglycolic acid: directing agent

\(30-60\) s

2-10 g min\(^{-1}\)

\(\approx 100\%\) yield

⇒ High crystallinity, shape control
**After sintering at 300/400°C under vacuum:**

Cold-compaction (hydraulic press) and sintering

- **Sulfur doping via the thioglycolic acid**
- **Protection against oxidation thanks to thioglycolic acid**
- **Bi$_2$Te$_3$: slight excess of Bi**

**WDX**

0.1-O.3 at.% Sulfur controlable through synthesis conditions

→ Sulfur doping via the thioglycolic acid
→ Protection against oxidation thanks to thioglycolic acid
→ Bi$_2$Te$_3$: slight excess of Bi

**TGA replaced by neodecanoate: n-type**

**S-doped Bi$_2$Te$_3$ (Bi-rich): n-type**

⇒ Importance of Sulfur doping

---

$\kappa$: 40-75%  
$L$: 60-75%  
\[ \Rightarrow \text{lower than bulk materials} \]

\[ \Rightarrow \text{attributed to nanostructuring} \]

10-100nm grains  
5-50nm inter and intragranular pores

\[ \Rightarrow \text{Electronic properties controlled by Sulfur doping} \]

\[ \Rightarrow \text{Thermal conductivity controlled by Nanostructuring} \]
Bi$_2$Te$_3$: 1-2 at. % Bi-rich

Sb$_2$Te$_3$: stoechiometric 1-5 at. % Bi-deficient

Bi$_2$Se$_3$: 0.1-0.3 at.% Sulfur

⇒ 25% higher than conventional alloys
⇒ 2-4 times higher than their bulk counterparts (same composition and stoichiometry)

⇒ High performances nanostructured materials through
  - nanostructuring
  - doping