Preparation and characterization of nanostructured thermoelectric materials

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Ca$_x$Co$_4$Sb$_{12}$/substrate films, BiSbTe nano-powders
Bi/PbTe/substrate films
Film specifications

- high quality films
- well-known thickness
- high density
- large grains
- smooth surfaces
- sharp interfaces - no interdiffusion
- no oxygen contamination

Pulsed laser deposition (PLD) for the synthesis of thermoelectric films

Stoichiometry of target restored
Lower deposition temperature
Experimental: pulsed laser deposition set-up

- **Nd : YAG LASER** (5 Hz, 10 ns)  
  $\lambda = 532$ nm

- Fast opening door
- Multiple target holder  
  Rotation: 9 r.p.m.
- Substrate heater & holder
- Gas inlet
- Molecular pump
- Ionic pump
- Electrical feedthrough
- Thermocouple feedthrough
- Motorized tables allowing the laser beam scanning along X,Y,Z
- Target PbTe
- Substrate
- Heating lamp
- 10$^{-7}$ - 10$^{-8}$ mbar
- Focusing lens
Experimental: pulsed laser deposition set-up

- Laser beam
- Nd:YAG laser
- Focusing lens
- x,y,z motorized tables
## Adjustable parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Laser</strong></td>
<td>Wavelength: 266, 532, 1064 nm (absorption)</td>
</tr>
<tr>
<td></td>
<td>Frequency: 2, 5 or 10 Hz (overlapping)</td>
</tr>
<tr>
<td></td>
<td>Output energy/focalisation (fluence)</td>
</tr>
<tr>
<td></td>
<td>Number of shots (thickness)</td>
</tr>
<tr>
<td><strong>Chamber</strong></td>
<td>Vacuum (static or <strong>dynamic</strong>)</td>
</tr>
<tr>
<td></td>
<td>Gas (static or dynamic)</td>
</tr>
<tr>
<td><strong>Target</strong></td>
<td>Polycrystalline self-made ingots</td>
</tr>
<tr>
<td></td>
<td>Diameter (12-19 mm)</td>
</tr>
<tr>
<td></td>
<td>Rotation speed</td>
</tr>
<tr>
<td><strong>Substrate</strong></td>
<td>Nature (amorphous, oriented)</td>
</tr>
<tr>
<td></td>
<td>Temperature (20-500°C)</td>
</tr>
<tr>
<td></td>
<td>Target-substrate distance (2-5 cm)</td>
</tr>
<tr>
<td><strong>Scanning</strong></td>
<td>Rate</td>
</tr>
</tbody>
</table>
Preparation of skutterudite thin films

**AIM:** Synthesis of high quality \textit{n}- and \textit{p}-type skutterudites films for their use in thermoelectric micro-devices. Study of the influence of many deposition parameters to achieve a single phase film having the skutterudite structure.

**MATERIAL:** Ca$_x$Co$_4$Sb$_{12}$ (\textit{n}-type), Ce$_x$Fe$_{3.5}$Co$_{0.5}$Sb$_{12}$ (\textit{p}-type)

**PARAMETER STUDIED:** wavelength: 266, 355 or 532 nm, density of energy: 2-5 J/cm$^2$, deposition temperature: 25-300°C,

**SUBSTRATE:** SiO$_2$(20 nm)/Si(100), quartz, glass
Influence of the deposition temperature (532 nm)

300°C: textured CoSb$_3$ + ?
240°C: CoSb$_3$ single phase
220°C: CoSb$_3$ + ?
25°C: amorphous

Thickness: 670 nm
Grain: > 500 nm
RMS = 16.1 nm

Thickness: 520 nm
Grain: ~ 100 nm
RMS = 38.4 nm

Decrease of film thickness and grain size when Ts $\uparrow$
Influence of the deposition temperature (266 nm)

Thickness: 70 nm
Grain size: < 80 nm
RMS: 12.7 nm

Comparison with 532 nm:

• No achievement of the skutterudite phase, whatever $T_s$ or fluence ($\neq$ from the literature)
• No reduction of the droplet density
• Deposition rate about 10 times lower
The nature of the substrate is not significant.

The deposition temperature differs strongly according to the wavelength (150°C at 266 nm (UV) and 240°C at 532 nm (visible)).
Topography of n-type skutterudite films (AFM)

Quartz substrate: influence of wavelength

→ The films exhibit a low amount of droplets, especially when made from 532 nm, and are smooth (RMS ~ 10 nm).

→ The surface shows a well defined morphology.

→ Grain sizes are about 100 to 200 nm.

→ RMS does not depend on substrate nature.
Both $n$- and $p$-type materials show typical behaviours of semi-conductors.

The values of the $p$-type film are much lower than those of the $n$-type film, in agreement with the differences observed for the bulk materials.
The films exhibit the same type of conductivity as the target materials they are made from.

The preliminary results show that the carrier mobilities are as high as in bulk materials for the $p$-type films and much smaller than in bulk materials for the $n$-type films.
**Skutterudite films: conclusions**

→ The synthesis of skutterudite films revealed to be particularly sensitive to quite all deposition parameters we tested, but feasibility to make both \( n \)- and \( p \)-type materials by PLD has been proven.

→ The skutterudite phase could be achieved for the first time with the 532 nm wavelength, for a given density of energy (4 J/cm\(^2\)), deposition temperature (240°C), and base pressure (10\(^{-4}\) mbar). These films exhibit less droplets and a smoother surface than films prepared in the UV range (for equivalent film thickness), contrarily to many materials.

→ The first transport property measurements showed that the films behaves similarly with temperature than the bulk materials.

Further work:

→ Try to realise a thermoelectric micro-generator made from both the \( n \) and \( p \)-type skutterudites synthesized.
Nanostuctured bulk materials: Aim

Nano-structured bulk materials with enhanced thermoelectric performance

High yield production of nano-particles of thermoelectric materials

- size as small as possible
- narrow particle size distribution
- composition close to that of the starting material

Pulsed laser ablation in a liquid media
(simple, versatile, no chemical reagents)

Materials: $n$- and $p$-type $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$

Physico-chemical characterization of the produced powders
Pulsed laser ablation in a liquid media: principle

Diagram:
- Laser beam
- Focusing lens
- Glass vessel
- Liquid media
- Target
- Nano-particles
Experimental set-up

- Nd:YAG laser
- Magnetic stirring
- Laser beam
- Target + Liquid
- Focusing lens
- x,y motorized tables (crenel-like scanning)
- (agglomeration avoiding, less particles-beam interactions)
### Experimental parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>laser</strong></td>
<td>532 or 1064 nm</td>
</tr>
<tr>
<td></td>
<td>2, 5 or 10 Hz</td>
</tr>
<tr>
<td></td>
<td>1 - 20 J/cm(^2)</td>
</tr>
<tr>
<td></td>
<td>1 - 36 000 shots</td>
</tr>
<tr>
<td><strong>target</strong></td>
<td>polycrystalline</td>
</tr>
<tr>
<td></td>
<td>(n (\text{Bi}<em>{0.95}\text{Sb}</em>{0.05})<em>2(\text{Te}</em>{0.95}\text{Se}_{0.05})_3)</td>
</tr>
<tr>
<td></td>
<td>(\rho (\text{Bi}<em>{0.2}\text{Sb}</em>{0.8})_2\text{Te}_3)</td>
</tr>
<tr>
<td><strong>liquid</strong></td>
<td>water, ethanol, n-heptane</td>
</tr>
<tr>
<td></td>
<td>1 or 2 cm height</td>
</tr>
<tr>
<td><strong>scanning rate</strong></td>
<td>0.5 or 2 mm/s</td>
</tr>
</tbody>
</table>
Yield optimization: influence of the laser frequency

*n*-type, 532 nm, water, 2.6 J/cm², 1 hour

Strong influence of the laser frequency

- **2 Hz**: no overlapping between 2 consecutive shots
- **5 Hz**: 50 % overlapping
- **10 Hz**: 80 % overlapping (2 mm/s)
- **10 Hz**: 90 % overlapping (0.5 mm/s)

→ **5 Hz, 2 mm/s**

Saturation limit: ~ 3 mg → 70 µg/cm³
Yield optimization: influence of the fluence

1064 nm, water, 5 Hz

Density of energy $\uparrow$ mass ablated $\uparrow$ (limitation 300 mJ)

Saturation limit: $\sim 10 \text{ mg} \rightarrow 220 \ \mu\text{g/cm}^3 \rightarrow \text{IR}$

$p$-type $\neq n$-type
Cristallographic structure: influence of the fluence

1064 nm, 18000 shots, 2 mm/s

**n-type**

Achievement of the same phase as the target

**p-type**

Achievement of a single phase but different from the target

or

Presence of multiple phases
### Chemical composition (EPMA)

1064 nm, 18000 shots, 2 mm/s

<table>
<thead>
<tr>
<th></th>
<th>Bi</th>
<th>Te</th>
<th>Sb</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-target</td>
<td>36.5</td>
<td>59.4</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>$n$-powders</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>water, 100 mJ</td>
<td>38.2</td>
<td>58.2</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>water, 300 mJ</td>
<td>38.7</td>
<td>57.8</td>
<td>1.6</td>
<td>1.9</td>
</tr>
<tr>
<td>$p$-target</td>
<td>7.6</td>
<td>60.7</td>
<td>31.7</td>
<td>-</td>
</tr>
<tr>
<td>$p$-powders</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>water, 60 mJ</td>
<td>8.0</td>
<td>60.8</td>
<td>31.3</td>
<td>-</td>
</tr>
</tbody>
</table>
**Morphology**

1064 nm, 18000 shots, 60 mJ, 2 mm/s

*n*-type

$p$-type

Mean particle size

TEM: 28 nm (200 shots)

XRD: 35 nm (18000 shots)
Summary

Proof-of-principle: pulsed laser ablation in a liquid media is efficient to synthesize nano-powders of complex materials.

$n$-type \((\text{Bi}_{0.95}\text{Sb}_{0.05})_2(\text{Te}_{0.95}\text{Se}_{0.05})_3\) can be synthesized in water.

\(p\)-type \((\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3\) is more difficult to synthesize.
(different absorption coefficient, different interaction with the solvent).

Each parameter studied has an influence (tailor as a function of we want):
- wavelength \(\rightarrow\) saturation limit of particles in the solution, size, composition
- solvent \(\rightarrow\) height: yield,
  nature: crystallographic phase, size, agglomeration aptitude
- energy \(\rightarrow\) yield, size, crystallographic phase

Problems: low ablation yield, no \(p\)-type, ‘large’ particle size distribution (laser-powder interaction ?), inflammability and recuperation of the solvent, oxidation.
New process diagram

- n-type or p-type ingot
- crushing
- sieving
- XRD analyses
- SEM analyses
- TEM analyses
- Laser gen.
- prism
- Distilled water
- 10 Hz 532 nm 36000 shots
New experimental

Initial powders in distilled water (small diameter vessel, 10 Hz)

→ 3 magnets

Guiding beam for adjusting the laser beam position (excentered position)
Influence of the number of shots: sedimentation test

*p*-type, 532 nm, 300 mJ, 30 min test

- a: initial powders
- b: 9 000 shots
- c: 18 000 shots
- d: 27 000 shots
- e: 36 000 shots

Duration of sedimentation increases as a function of the number of shots:
- → the weight and therefore the size of the generated particles become lower,
- → more and more initial particles are broken.
Effect of the laser beam on the particles morphology

*p-type, 532 nm, 300 mJ, 36 000 shots*

Initial sieved powders: diameter is in the range of 1-17 µm and 2.5 µm in average

After laser treatment: nanopowders of size less than 30 nm
Influence of the composition on the particle size

532 nm, 200 mJ, 36 000 shots

n-type nano-powders

p-type nano-powders
Influence of the composition on the particle size

532 nm, 200 mJ, 36 000 shots

\textit{n-type}: diameter in the range of 2.5–22.5 nm and 6 nm in average

\textit{p-type}: diameter in the range of 2.5–47.5 nm and 10 nm in average
Crystallographic structure

532 nm, 36 000 shots

$n$-type $(\text{Bi}_{0.95}\text{Sb}_{0.05})_2(\text{Te}_{0.95}\text{Se}_{0.05})_3$

$p$-type $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$

→ no significant difference as a function of output energy for both type
→ $n$-type: single phase
→ $p$-type: unknown phase, disappearing after annealing at 180°C
Conclusion

By comparison to the production of nano-powders from a bulk target, the use of initial micro-sized powders leads to:

→ smaller particles,

→ improved production yield,

→ improved crystalline quality of the p-type nano-powders (annealing),

→ no inflammability problem (use of water).
Now

Acrylic box with powder circulation in water

Use of a new fabrication cell to produce nano-powders with high yield to make:

• nano-structured bulk materials (SPS) to test the thermoelectric performance (electrical and thermal conductivities, thermopower, \( \rightarrow \) improvement?)

• thin films directly from the solution by electrophoresis and test their thermoelectric performance (use in micro-devices: \( \mu \)-generators or \( \mu \)-refrigerators)
PbTe-Bi nano-composites: influence of bi-layers number (BaF$_2$, 150°C)

→ Smoothening of the surface as the number of bi-layers increases
→ Obtaining of the (111) texture
Transport properties of PbTe films and Bi/PbTe nano-composites
(T_s = 150°C, F = 4 J/cm²)

<table>
<thead>
<tr>
<th></th>
<th>Resistivity [µΩ.m]</th>
<th>Seebeck [µV.K⁻¹]</th>
<th>Power factor [µW.m⁻¹.K⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe/BaF₂</td>
<td>45</td>
<td>-247</td>
<td>1355 (n=4.9x10¹⁷ cm⁻³)</td>
</tr>
<tr>
<td>20 (PbTe/Bi/BaF₂)</td>
<td>32</td>
<td>-223</td>
<td>1554 (n=2.3x10¹⁸ cm⁻³)</td>
</tr>
<tr>
<td>PbTe/glass</td>
<td>14</td>
<td>-156</td>
<td>1760 (n=2.0x10²⁰ cm⁻³)</td>
</tr>
<tr>
<td>20(PbTe/Bi/glass)</td>
<td>8</td>
<td>-118</td>
<td>1780</td>
</tr>
</tbody>
</table>
Thermal cycling of PbTe films and Bi/PbTe nanocomposites

The PbTe films do not withstand thermal cycling ...

...but the Bi/PbTe nanocomposites do!