Preparation and characterization of nanostructured thermoelectric materials

Nancy-Université

Laboratoire de Physique des Matériaux, UMR 7556
Ecole Nationale Supérieure des Mines de Nancy, France

A. Dauscher, B. Lenoir, D. Colceag, V. Kosalathip,
C. Candolfi, V. Da Ros

$Ca_xCo_4Sb_{12}$/substrate films , BiSbTe nano-powders

Bi/PbTe/substrate films

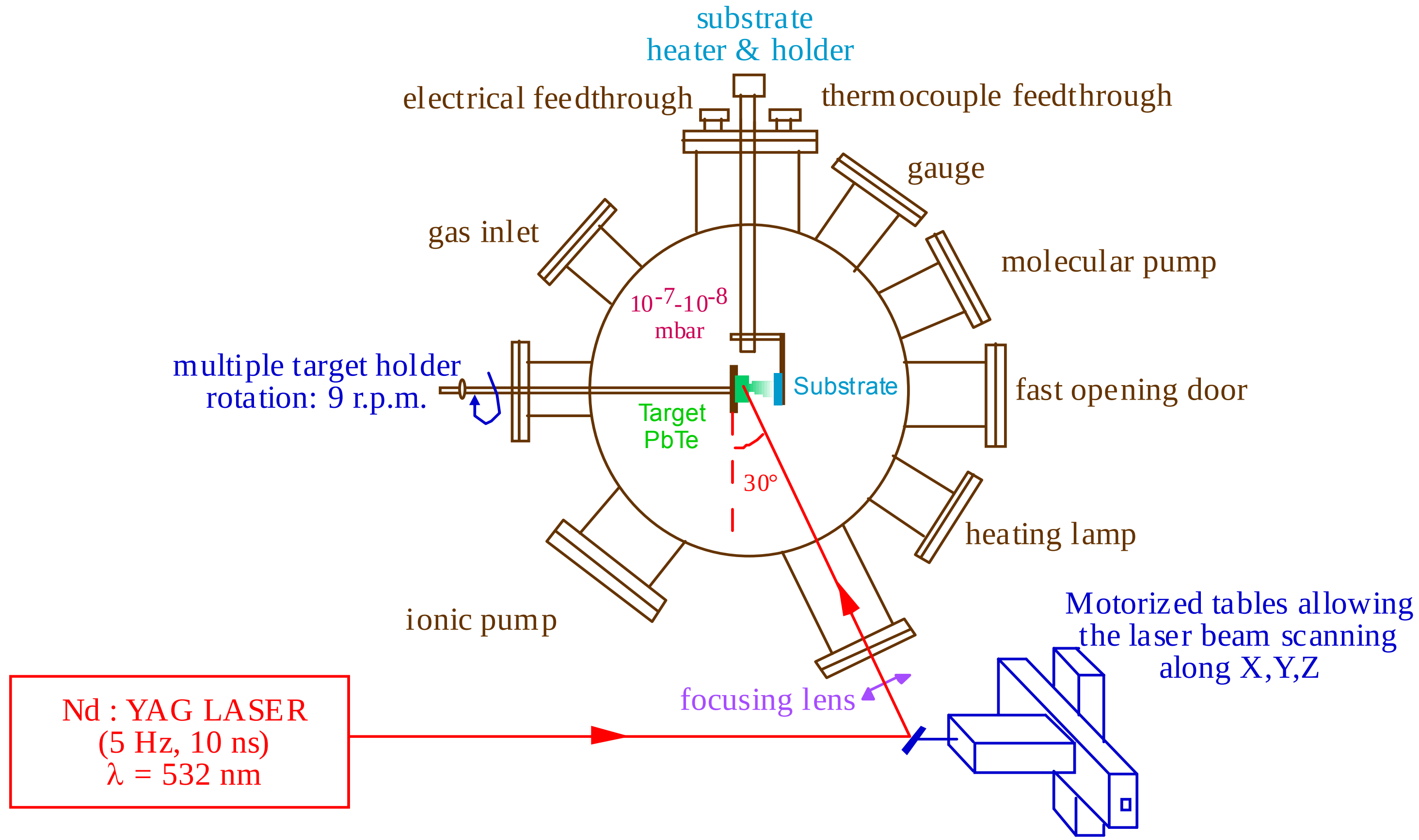
Film specifications

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

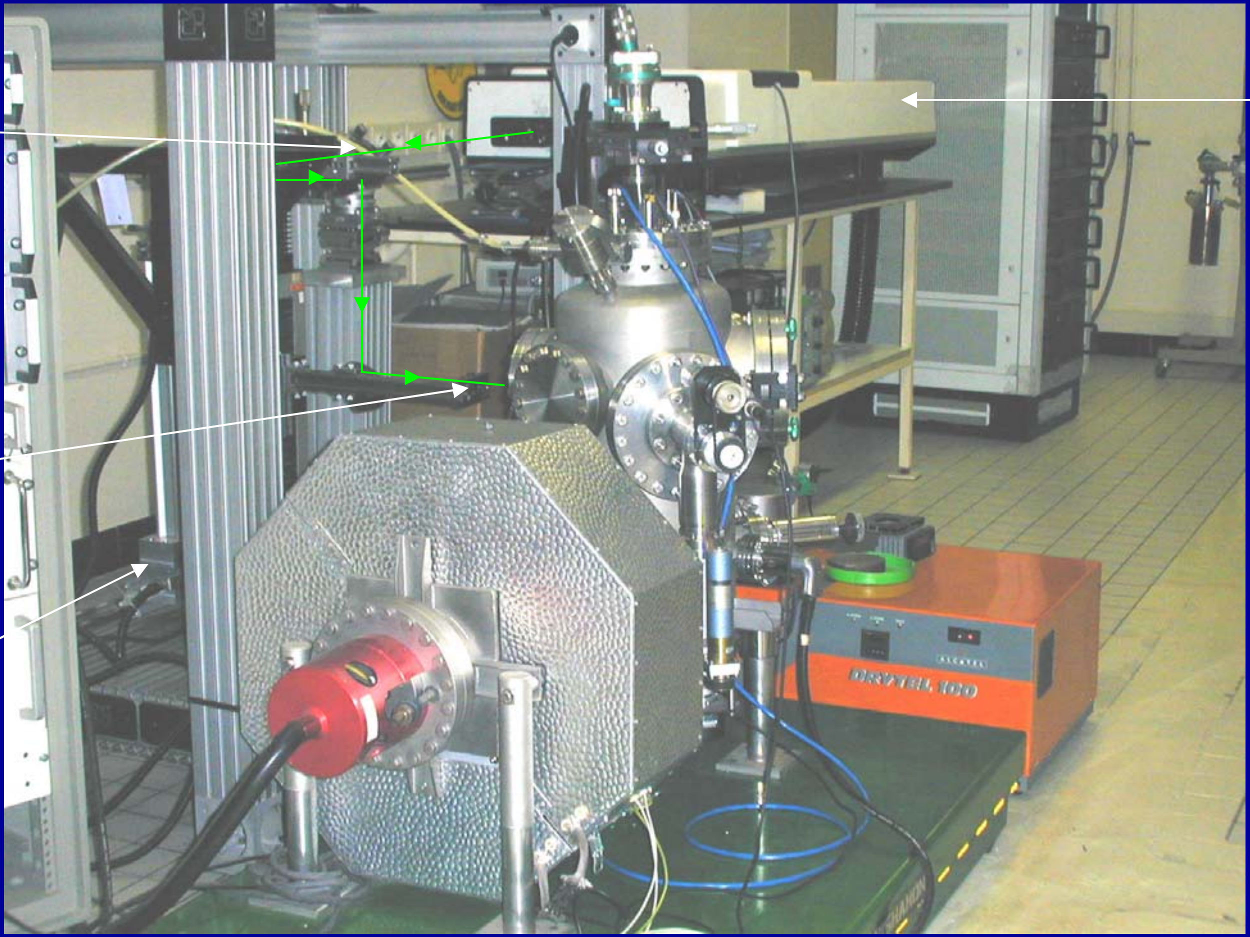
Pulsed laser deposition (PLD) for the synthesis of thermoelectric films

Stoichiometry of target restored
Lower deposition temperature

Experimental: pulsed laser deposition set-up



Experimental: pulsed laser deposition set-up



Laser beam

Nd:YAG laser

Focusing lens

x,y,z motorized tables

Adjustable parameters

Laser	Wavelength: 266, 532, 1064 nm (absorption) Frequency: 2, 5 or 10 Hz (overlapping) Output energy/focalisataion (fluence) Number of shots (thickness)
Chamber	Vacuum (static or dynamic) Gas (static or dynamic)
Target	Polycrystalline self-made ingots Diameter (12-19 mm) Rotation speed
Substrate	Nature (amorphous, oriented) Temperature (20-500°C) Target-substrate distance (2-5 cm)
Scanning	Rate

Preparation of skutterudite thin films

AIM: Synthesis of high quality *n*- and *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.

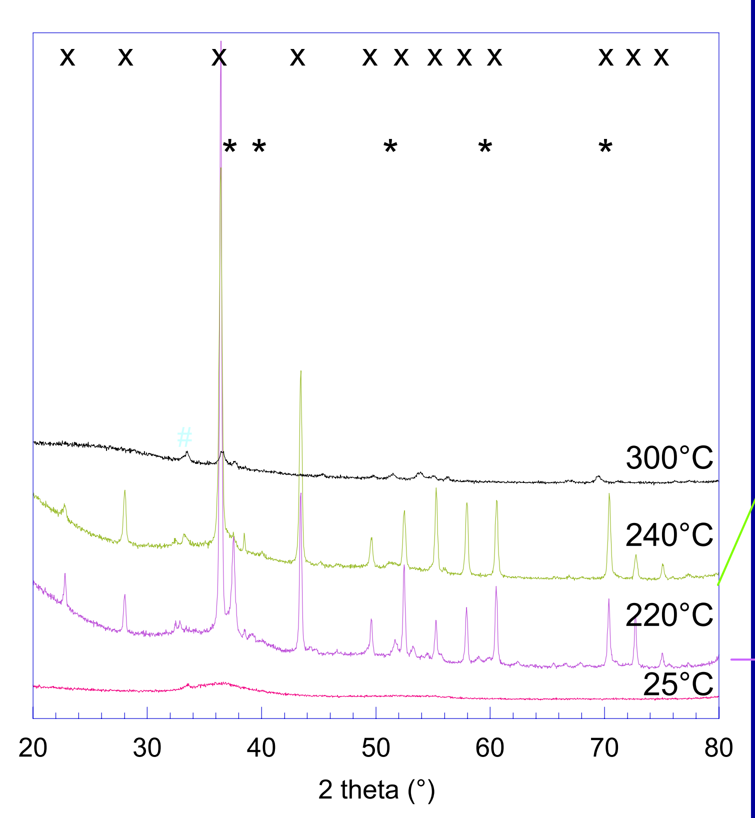
MATERIAL: $Ca_xCo_4Sb_{12}$ (*n*-type), $Ce_xFe_{3.5}Co_{0.5}Sb_{12}$ (*p*-type)

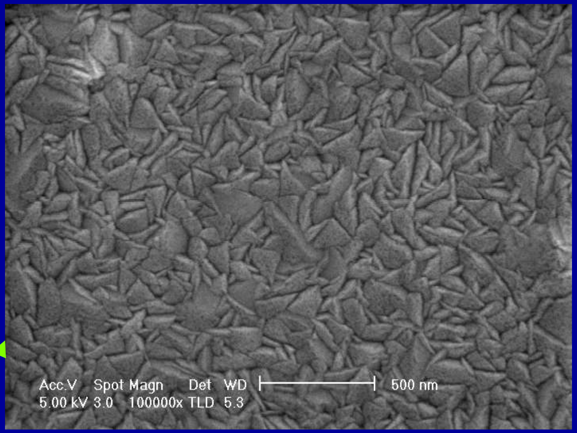
PARAMETER STUDIED: wavelength: 266, 355 or 532 nm, density of energy: 2-5 J/cm^2, deposition temperature: 25-300°C,

SUBSTRATE: SiO_2(20 nm)/Si(100), quartz, glass

Influence of the deposition temperature (532 nm)

X: $CoSb_3$, *: $CoSb_2$?, #: Sb

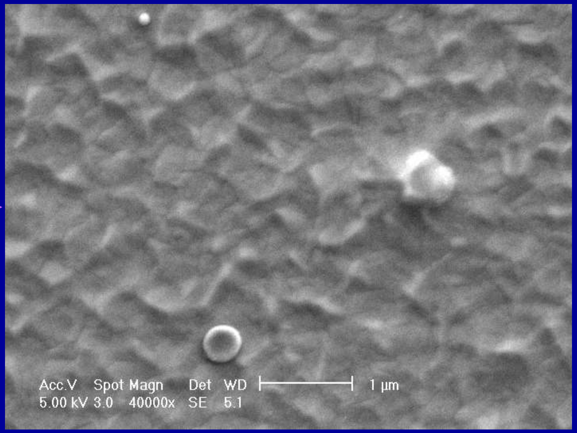




Thickness: 520 nm

Grain: ~ 100 nm

RMS = 38.4 nm



Thickness: 670 nm

Grain: > 500 nm

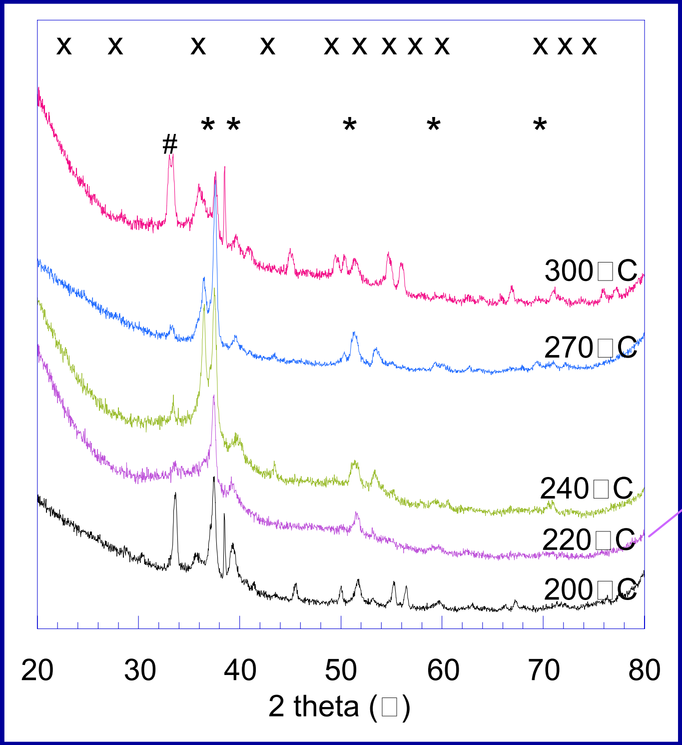
RMS = 16.1 nm

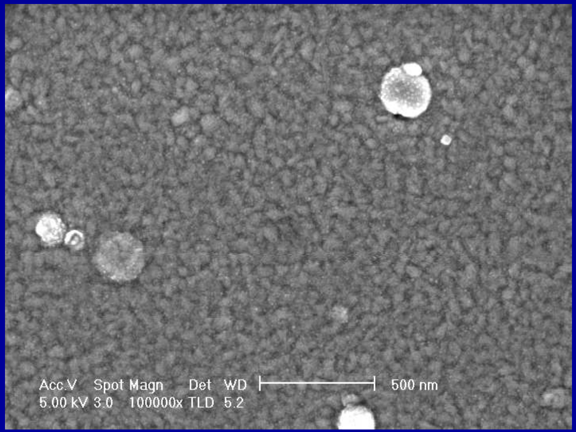
300°C: textured $CoSb_3$ + ?
240°C: $CoSb_3$ single phase
220°C: $CoSb_3$ + ?
25°C : amorphous

Decrease of film thickness and grain size when Ts ↑

Influence of the deposition temperature (266 nm)

X: $CoSb_3$, ∗: $CoSb_2$?, #: Sb



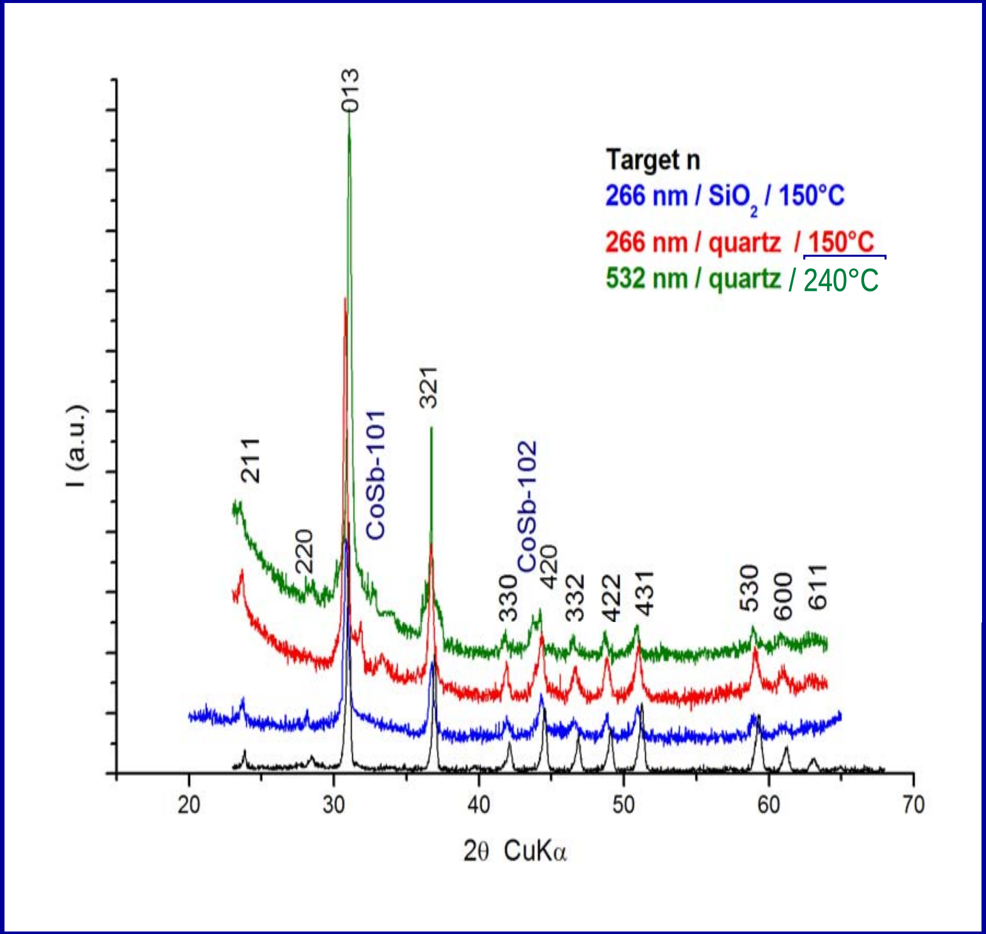


Thickness: 70 nm
Grain size: < 80 nm
RMS: 12.7 nm

Comparison with 532 nm:

- No achievement of the skutterudite phase, whatever T_s or fluence (≠ from the literature)
- No reduction of the droplet density
- Deposition rate about 10 times lower

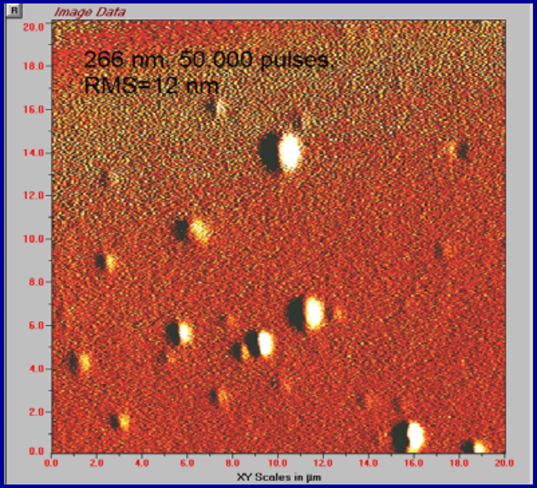
Influence of wavelength and substrate

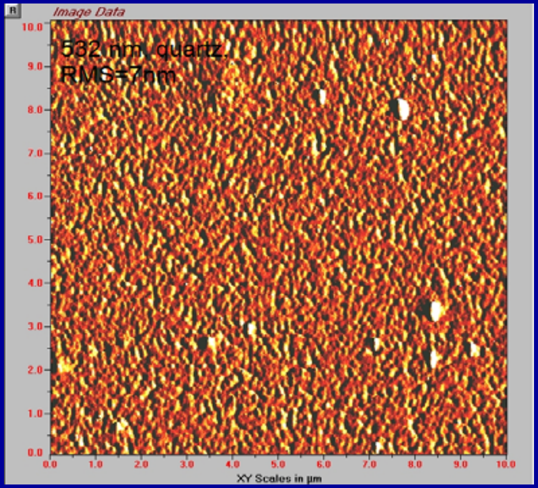


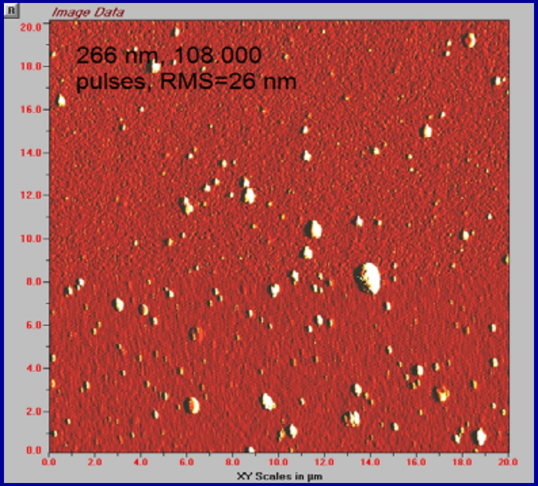
→ The nature of the substrate is not significative.

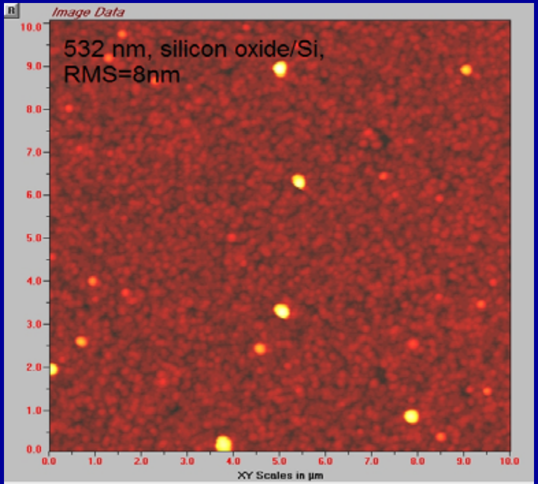
→ The deposition temperature differs strongly according to the wavelength (150°C at 266 nm (UV) and 240°C at 532 nm (visible)).

Topography of n-type skutterudite films (AFM)









Quartz substrate:
influence of thickness

50 000 pulses:
influence of substrate

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).

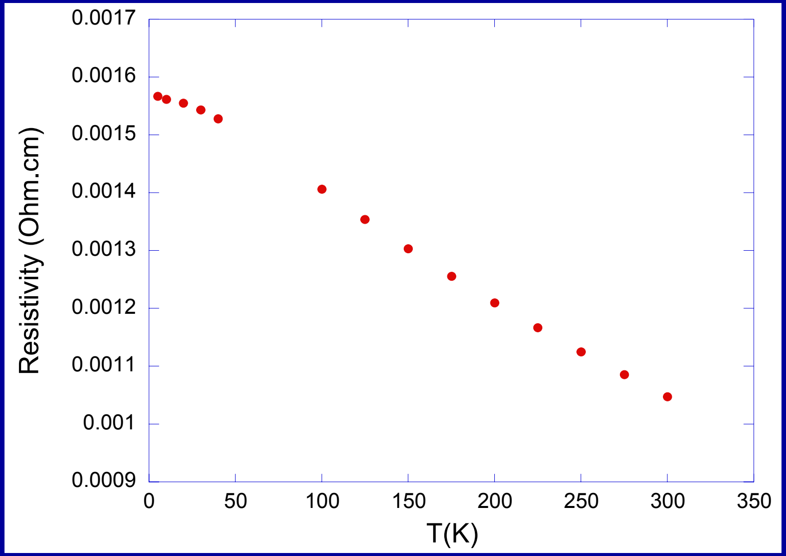
→ The surface shows a well defined morphology.

→ Grain sizes are about 100 to 200 nm.

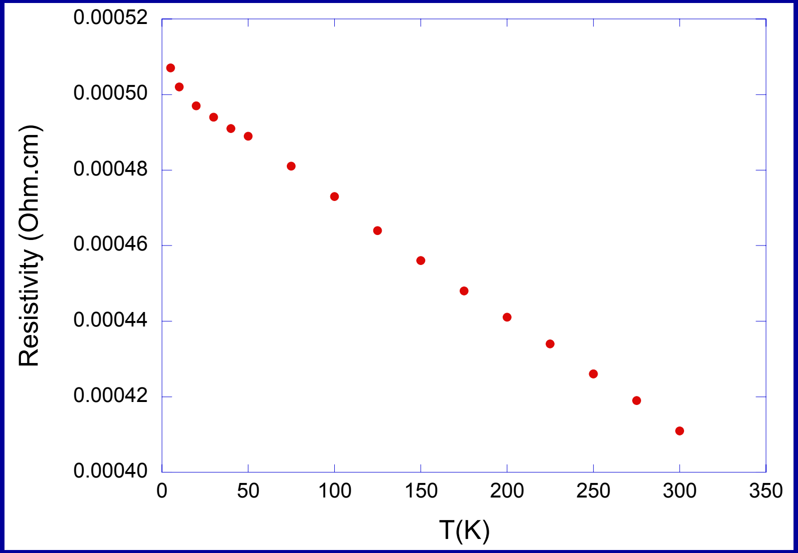
→ RMS does not depend on substrate nature.

Electrical resistivity of skutterudite films

n-type



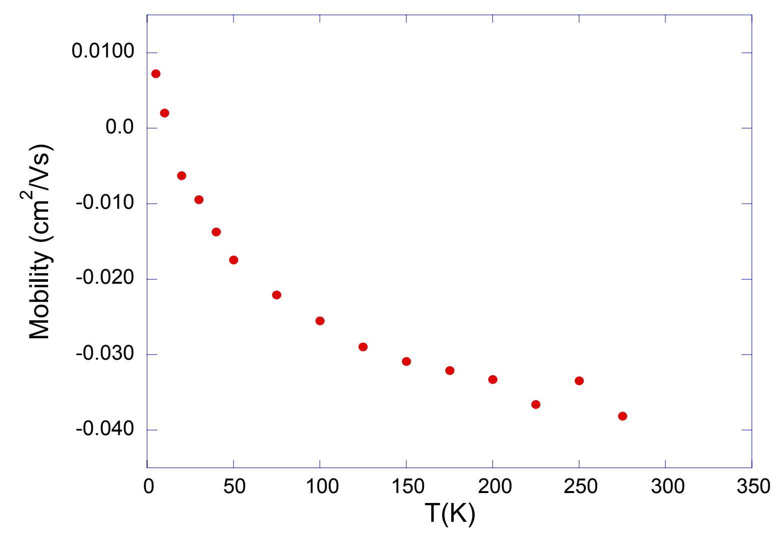
p-type

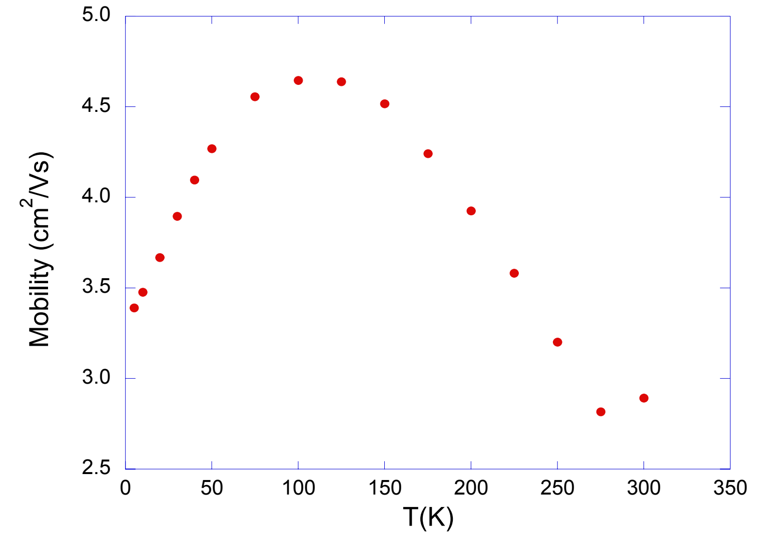


→ Both *n*- and *p*-type materials show typical behaviours of semi-conductors.

→ 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.

Carrier mobility of skutterudite films


n-type


p-type

→ 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 feasability 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

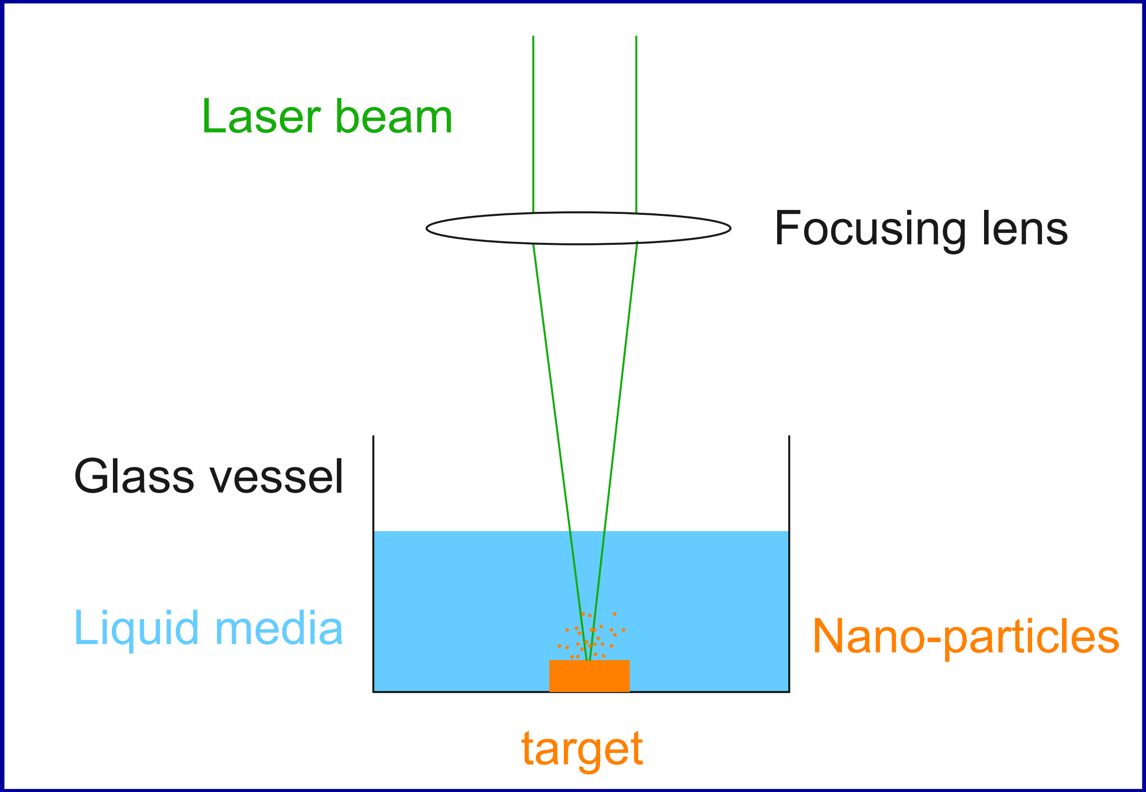
- size as small as possible
- narrow particle size distribution
- composition close to that of the starting material

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

Materials: *n*- and *p*-type $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$

Physico-chemical characterization of the produced powders

Pulsed laser ablation in a liquid media: principle



Experimental set-up

Nd:YAG laser

Focusing
lens

Laser beam

Target
+
Liquid

Magnetic strirring
(agglomeration avoiding,
less particles-beam interactions)

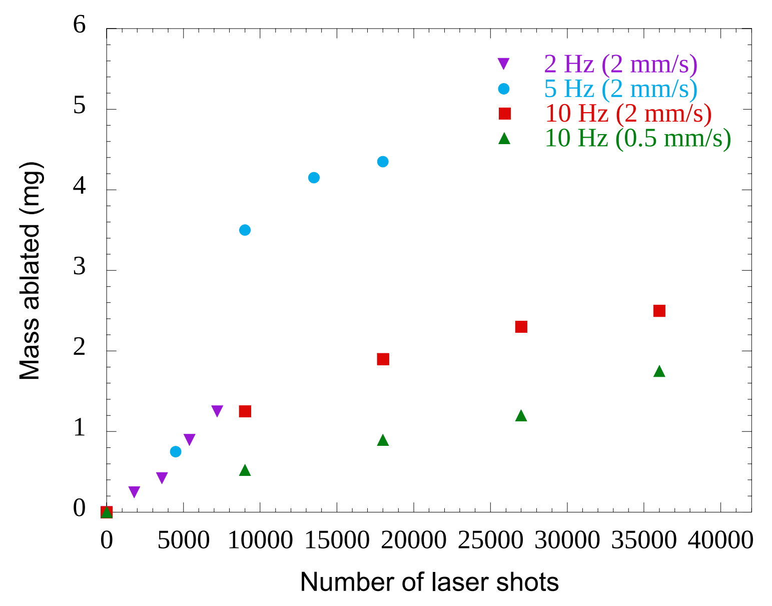
x,y motorized tables (crenel-like scanning)

Experimental parameters

laser	532 or 1064 nm 2, 5 or 10 Hz 1 - 20 J/cm^2 1 - 36 000 shots
target	polycrystalline *n* $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ *p* $(Bi_{0.2}Sb_{0.8})_2Te_3$
liquid	water, ethanol, n-heptane 1 or ~~2 cm~~ height
scanning rate	0.5 or 2 mm/s

Yield optimization: influence of the laser frequency

n-type, 532 nm, water, 2.6 J/cm^2, 1 hour



Strong influence of the laser frequency

2 Hz: no overlapping between 2 consecutive shots

5 Hz: 50 % overlapping → **5 Hz, 2 mm/s**

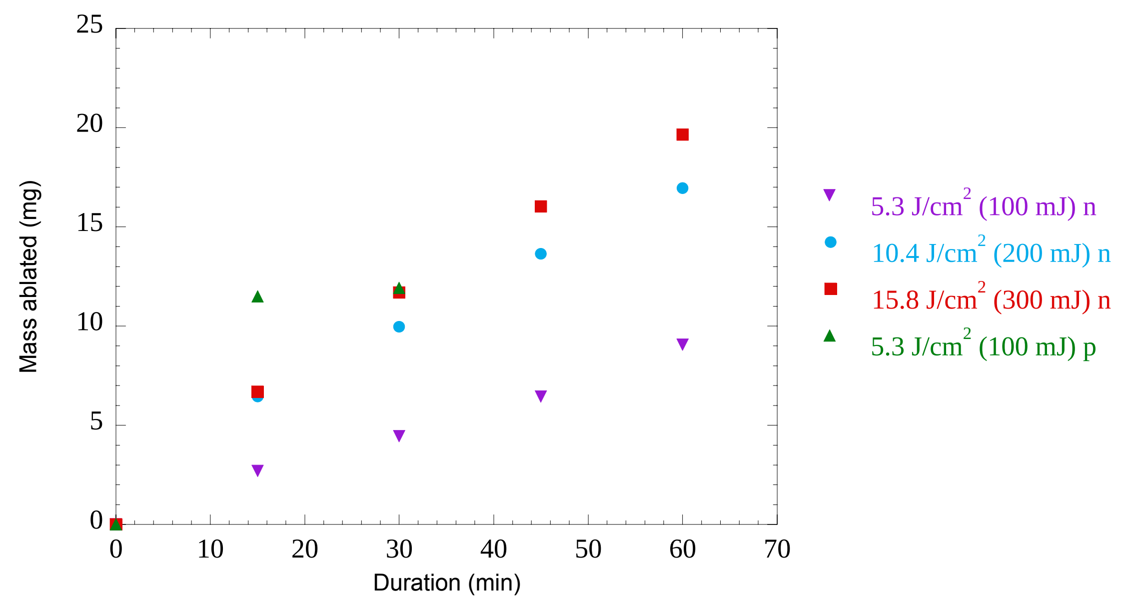
10 Hz: 80 % overlapping (2 mm/s)

10 Hz: 90 % overlapping (0.5 mm/s)

Saturation limit: ~ 3 mg → 70 μg/cm^3

Yield optimization: influence of the fluence

1064 nm, water, 5 Hz



Density of energy ↑mass ablated ↑ (limitation 300 mJ)

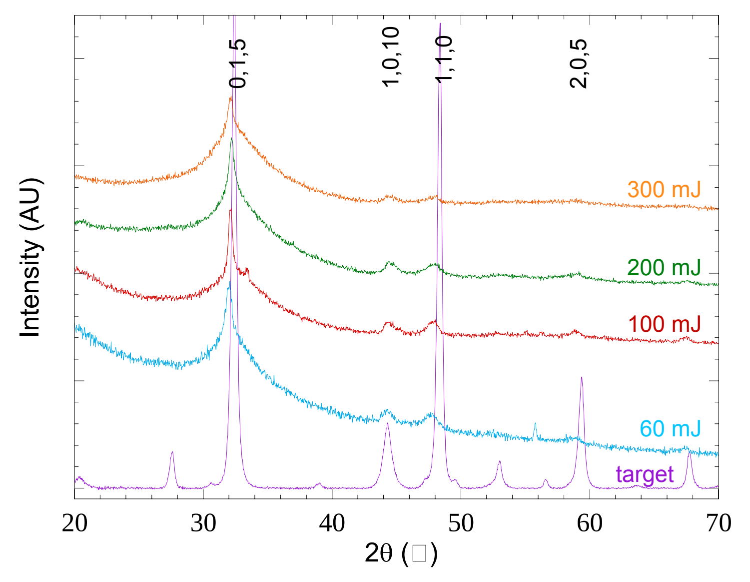
Saturation limit: ~ 10 mg → 220 μg/cm^3 → **IR**

p-type ≠ *n*-type

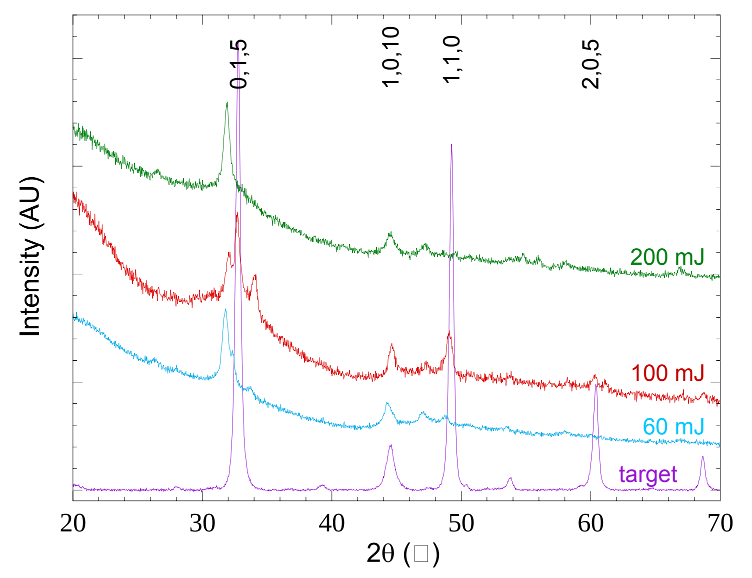
Cristallographic structure: influence of the fluence

1064 nm, 18000 shots, 2 mm/s

***n*-type**



***p*-type**



Achievement of the same phase as the target

Achievement of a single phase but different from the target

or

Presence of multiple phases

Chemical composition (EPMA)

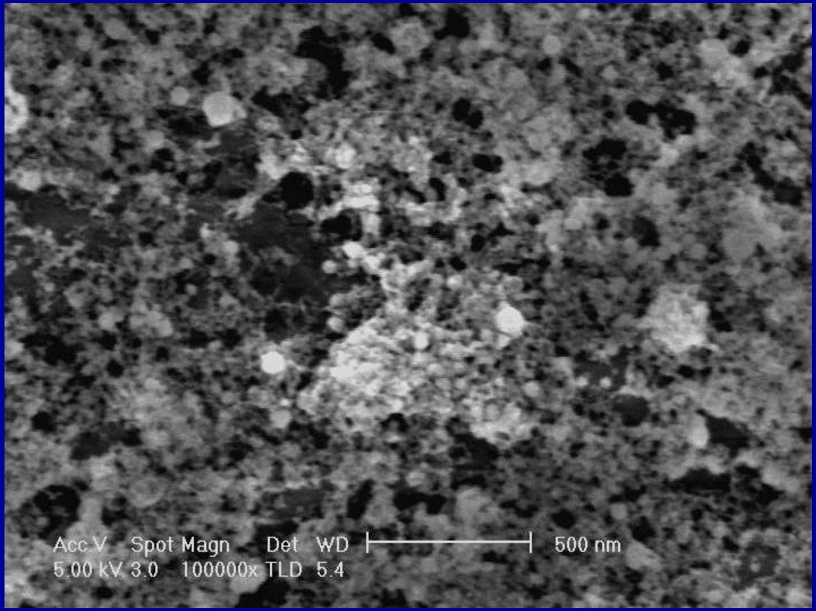
1064 nm, 18000 shots, 2 mm/s

	Bi	Te	Sb	Se
n-target	36.5	59.4	2.2	1.9
n-powders water, 100 mJ	38.2	58.2	1.8	1.8
n-powders water, 300 mJ	38.7	57.8	1.6	1.9
p-target	7.6	60.7	31.7	-
p-powders water, 60 mJ	8.0	60.8	31.3	-

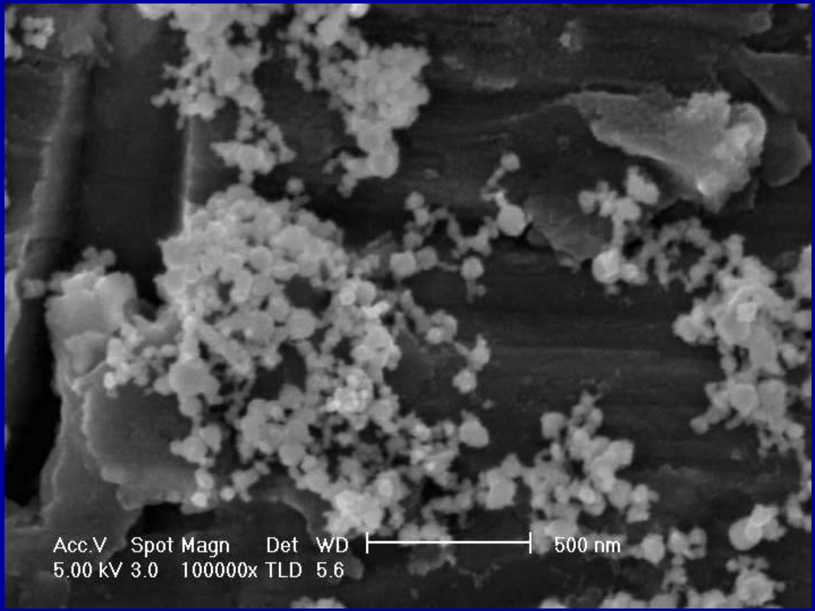
Morphology

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.

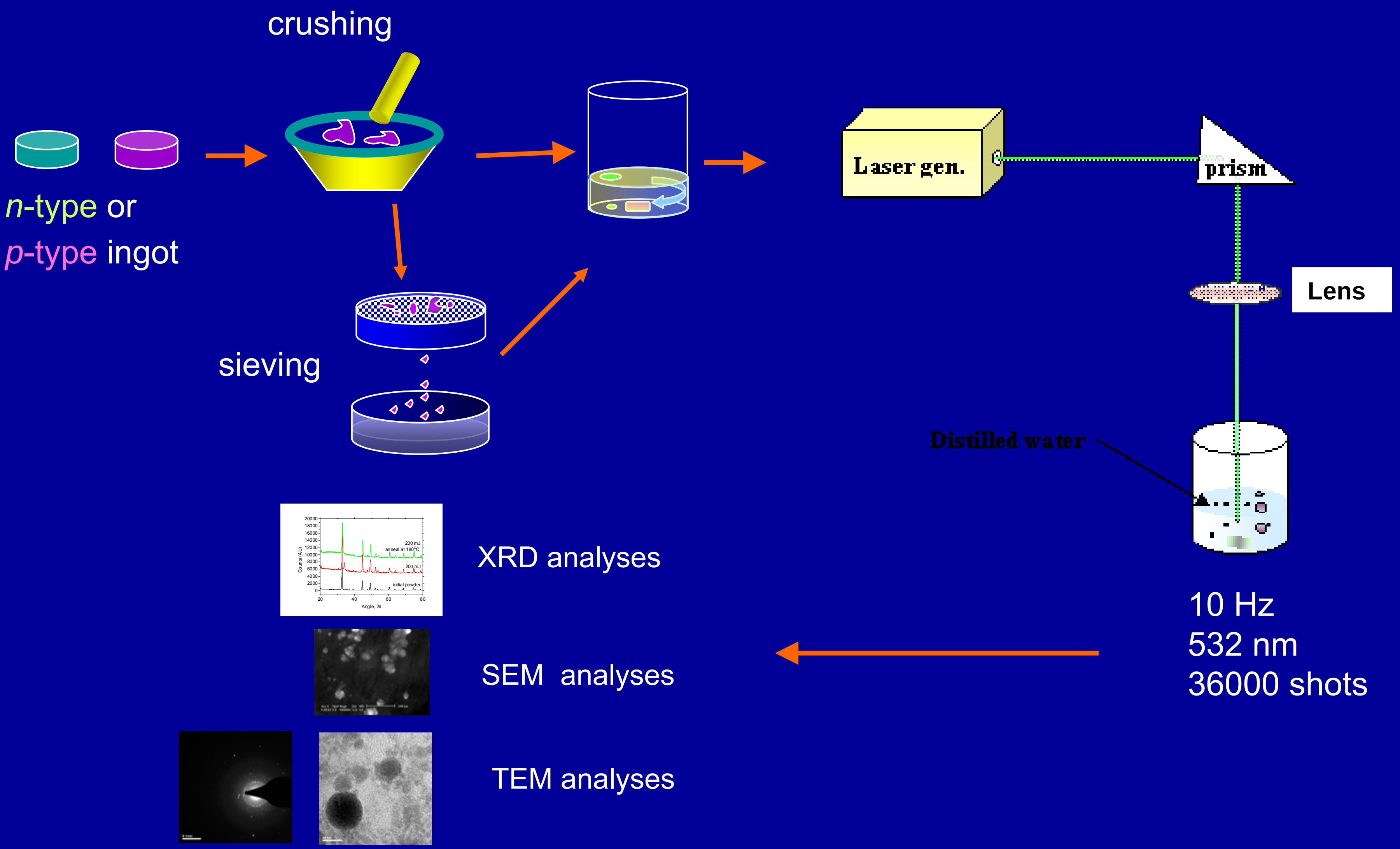
n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ can be synthesized in water.

p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ 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 → saturation limit of particles in the solution, size, composition
- solvent → height: yield,
  nature: crystallographic phase, size, agglomeration aptitude
- energy → 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



crushing

n-type or

p-type ingot

sieving

XRD analyses

SEM analyses

TEM analyses

10 Hz

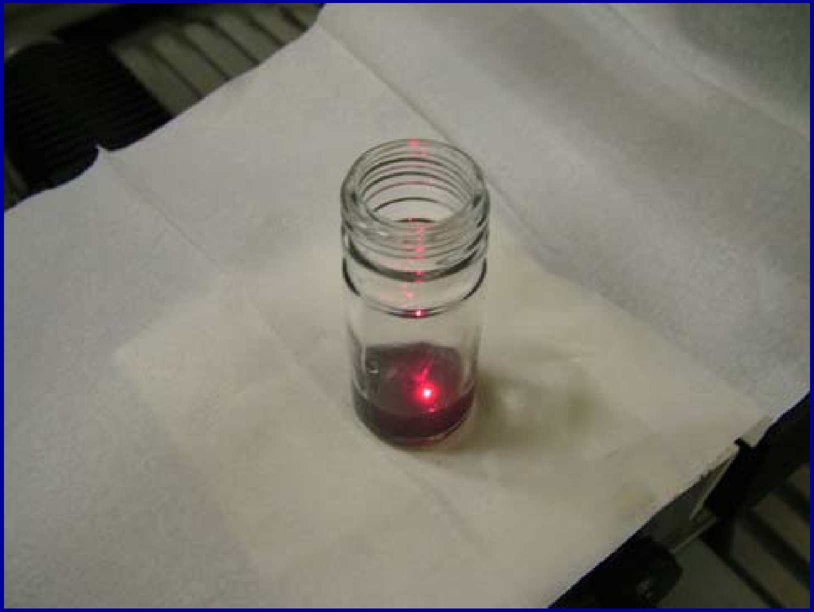
532 nm

36000 shots

New experimental

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

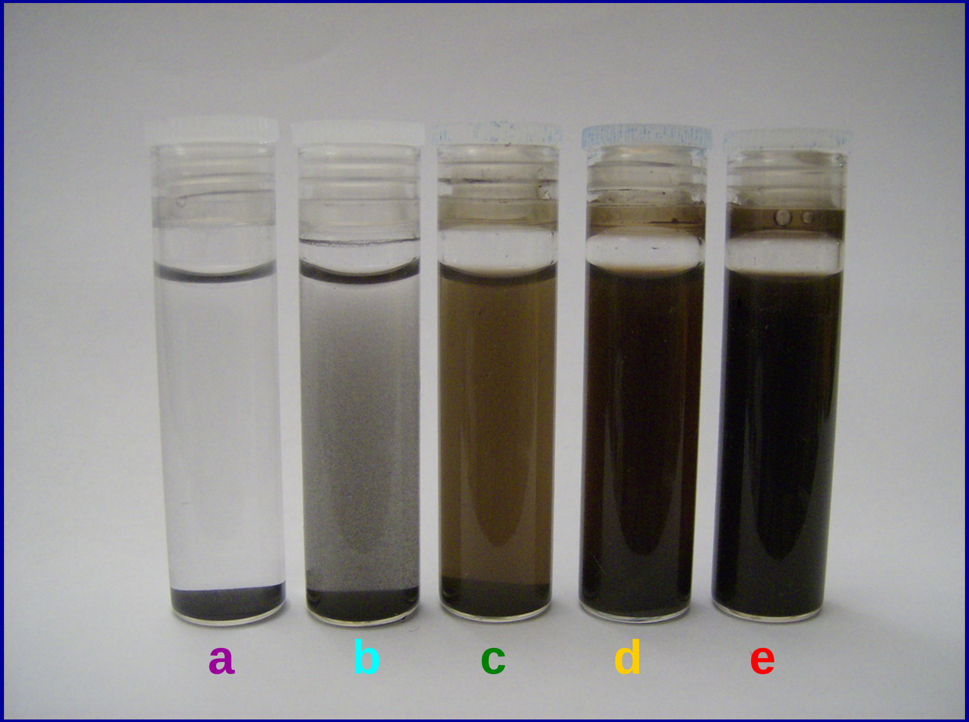
→ 3 magnets



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

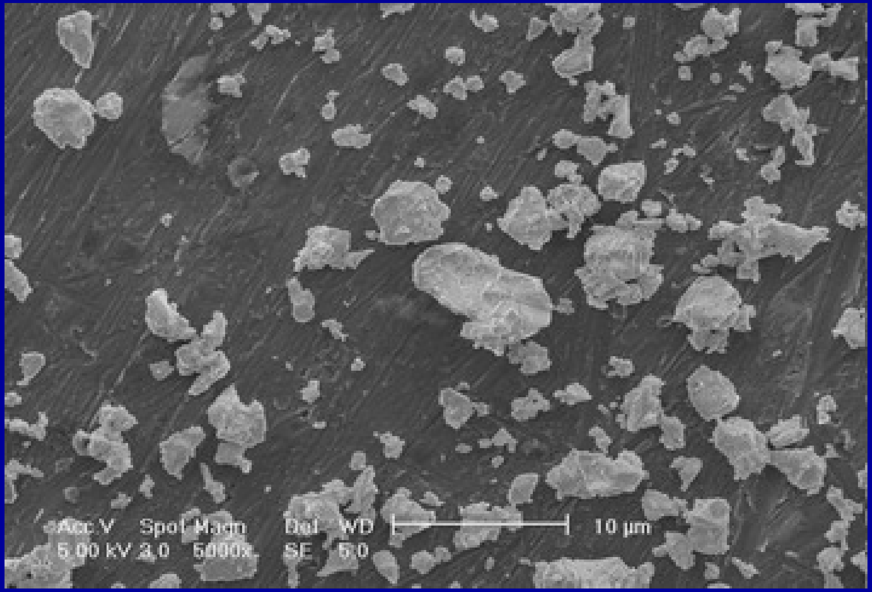
Duration of sedimentation increases as a function of the number of shots:

→ the weight and therefore the size of the generated particles become lower,

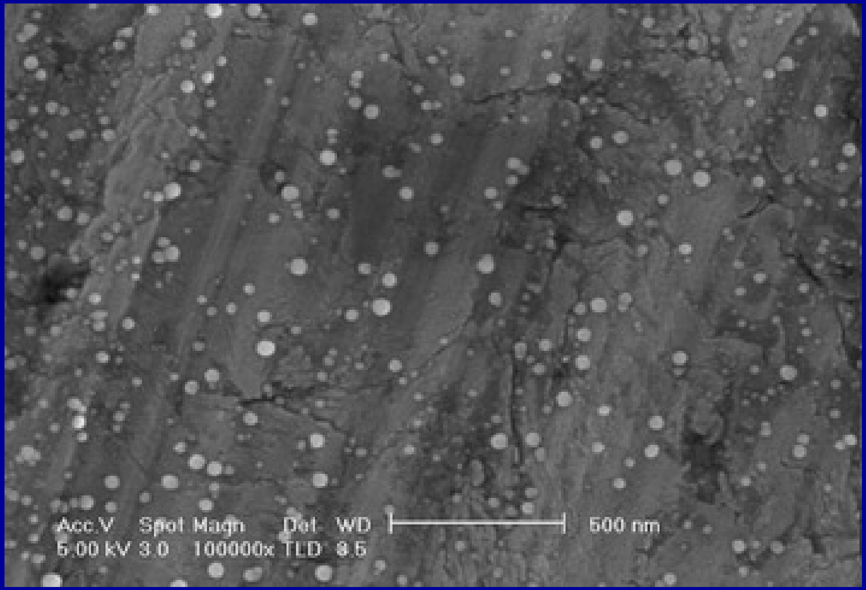
→ more and more initial particles are broken.

Effect of the laser beam on the particles morphology

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



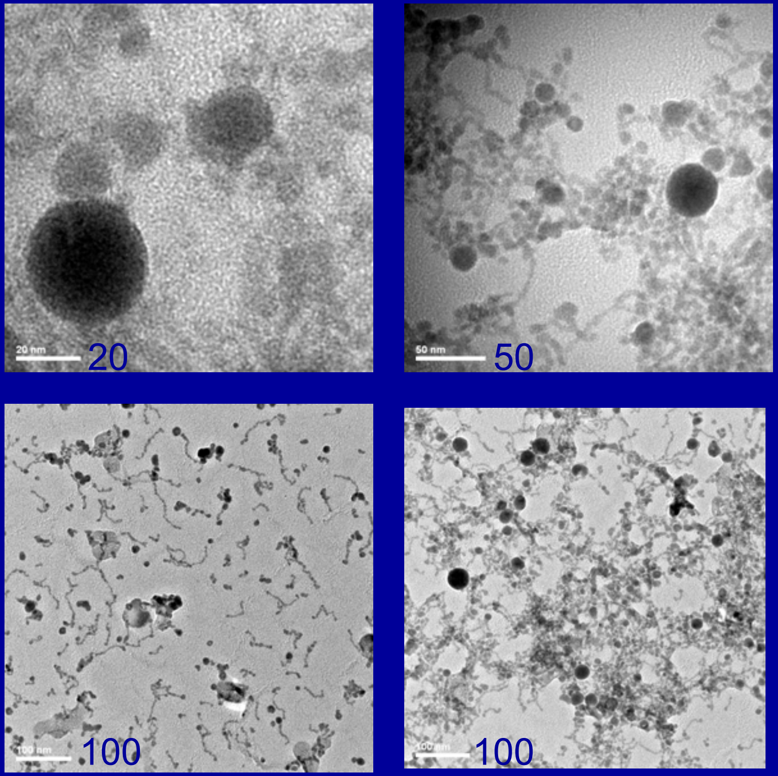
Initial sieved powders: diameter is in the range of 1- 17 µm and 2.5 µm in average



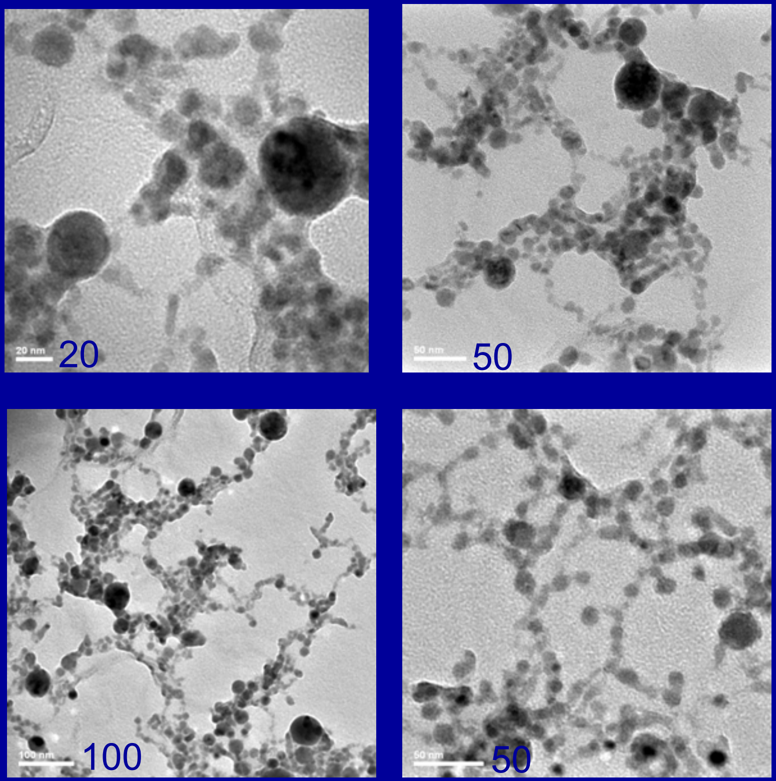
After laser treatment: nano-powders of size less than 30 nm

Influence of the composition on the particle size

532 nm, 200 mJ, 36 000 shots



n-type nano-powders

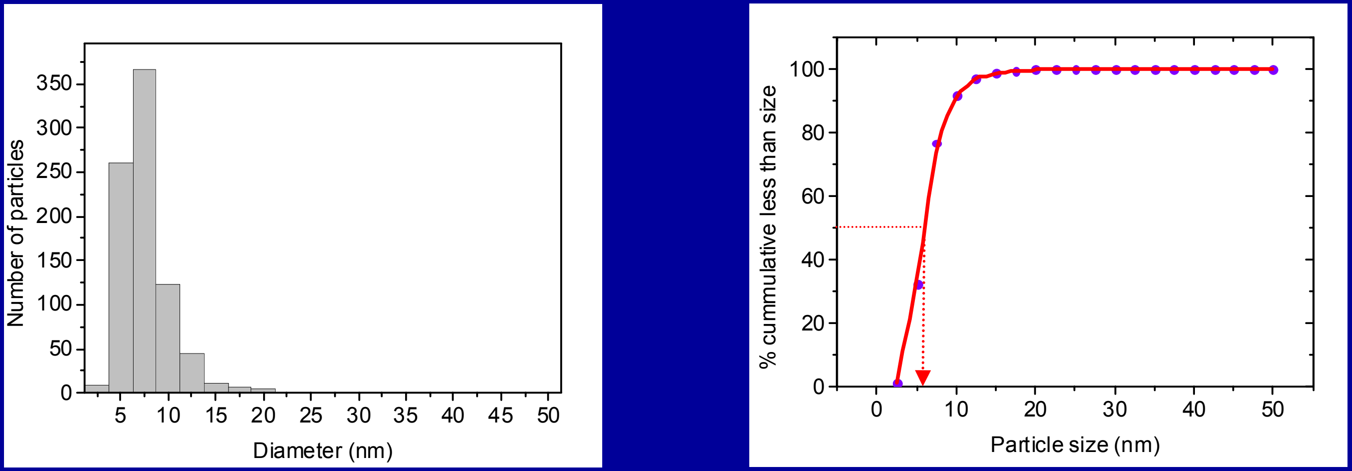


p-type nano-powders

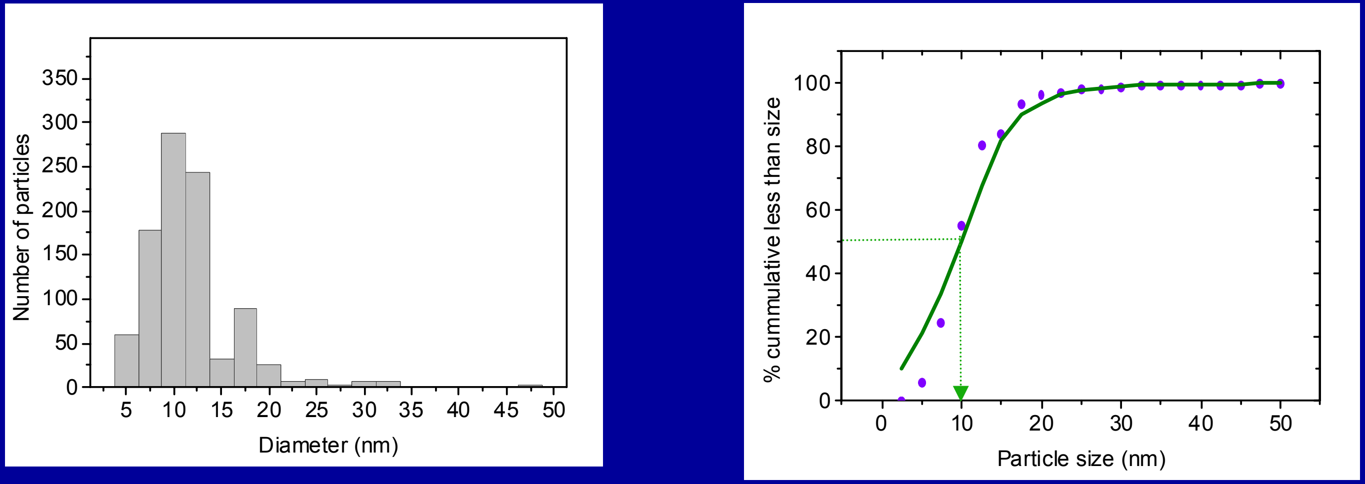
Influence of the composition on the particle size

532 nm, 200 mJ, 36 000 shots

n-type: diameter in the range of 2.5- 22.5 nm and 6 nm in average



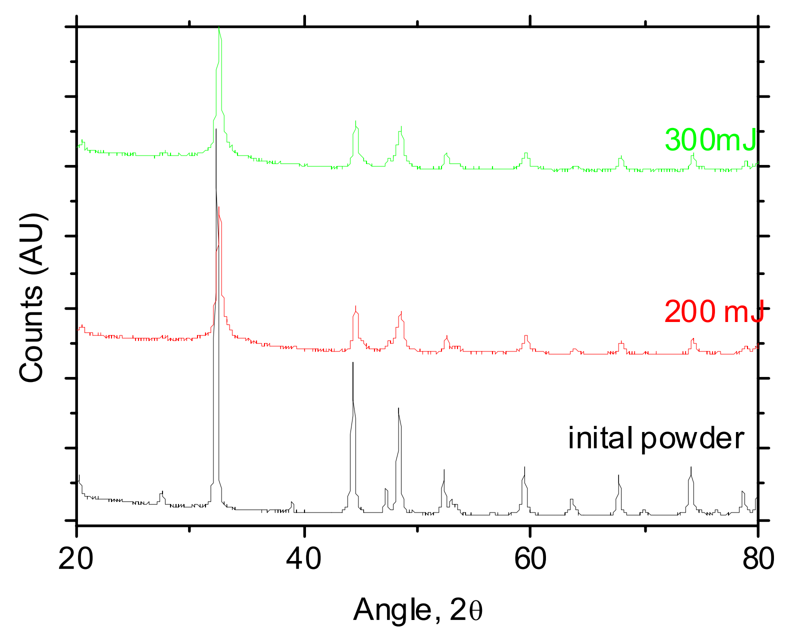
p-type: diameter in the range of 2.5 – 47.5 nm and 10 nm in average



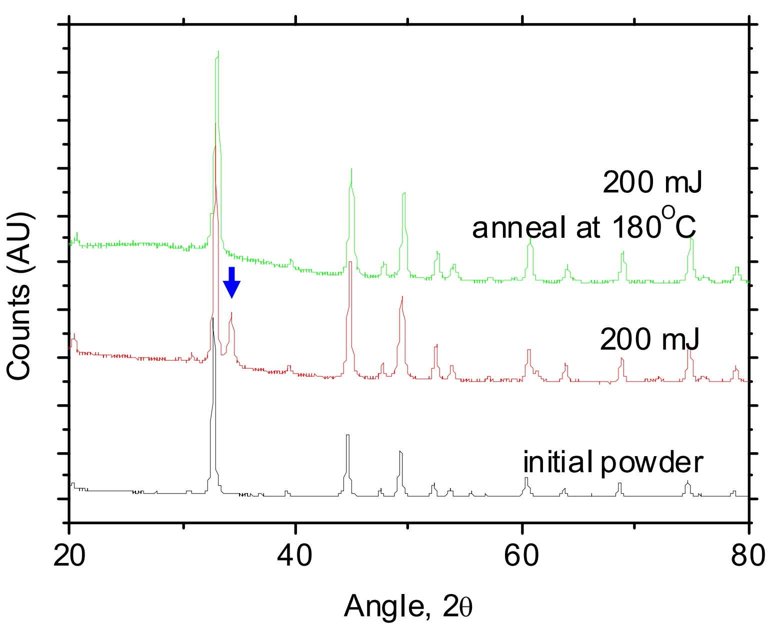
Crystallographic structure

532 nm, 36 000 shots

n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$



p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$



→ 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,

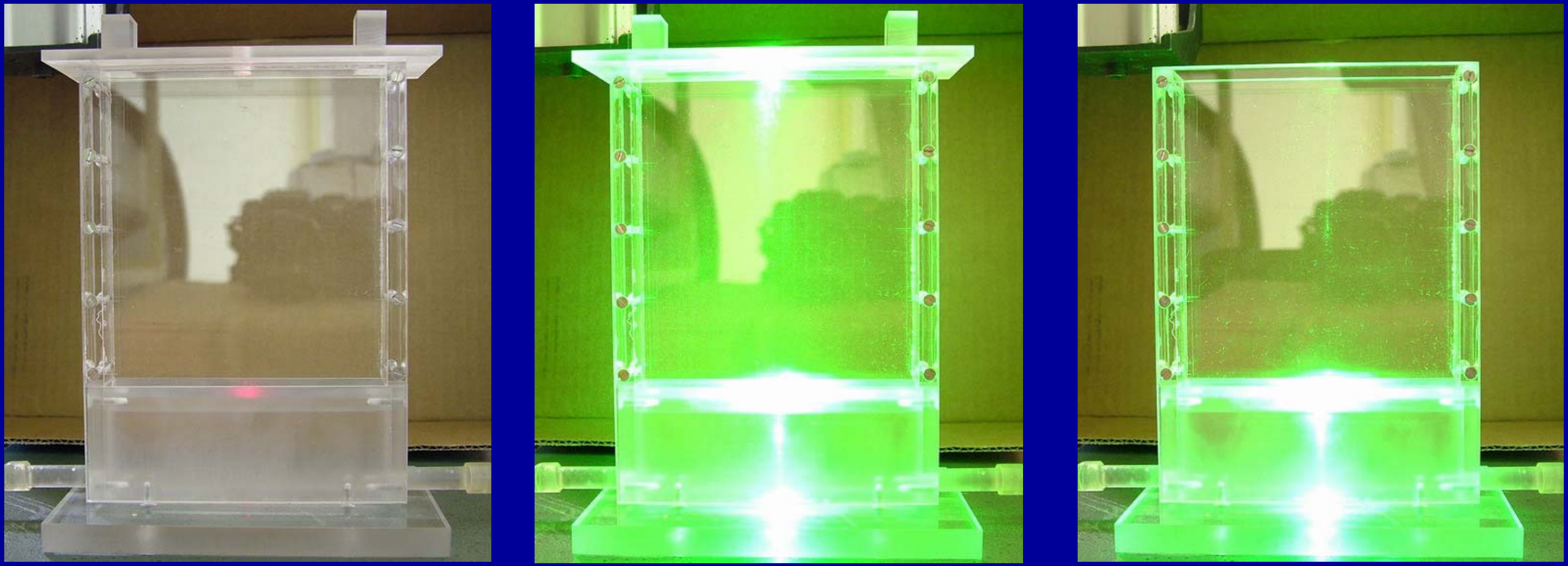
→ improved production yield,

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

→ no inflammability problem (use of water).

Now

Acrylic box with powder circulation in water



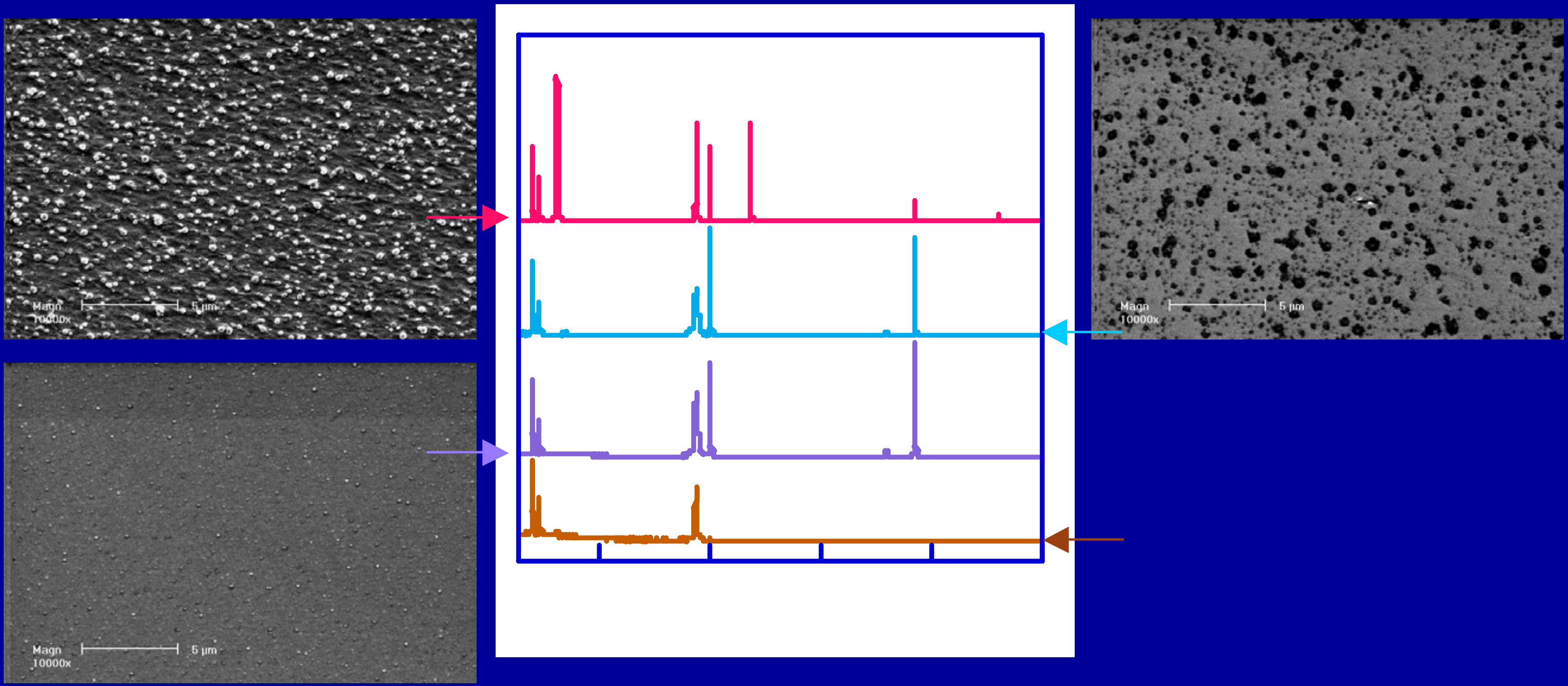
Use of a new fabrication cell to produce nano-powders with high yield to make:

- nano-structured bulk materials (SPS) to test the thermoelectric performance (electrical and thermal conductivities, thermopower, →improvment?)

- thin films directly from the solution by electrophoresis and test their thermoelectric performance (use in micro-devices: μ-generators or μ-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

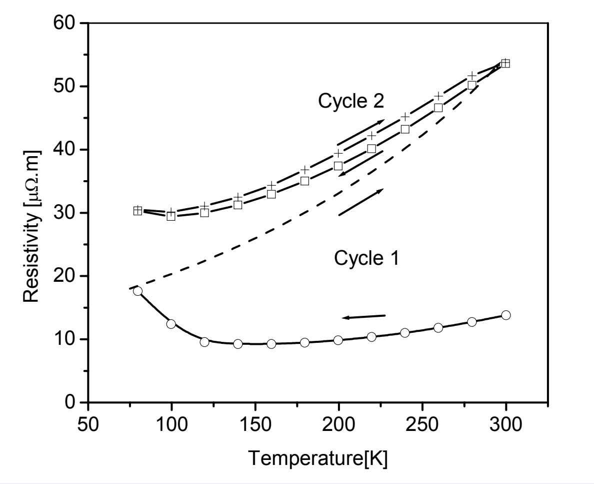
Transport properties of PbTe films and Bi/PbTe nano-composites

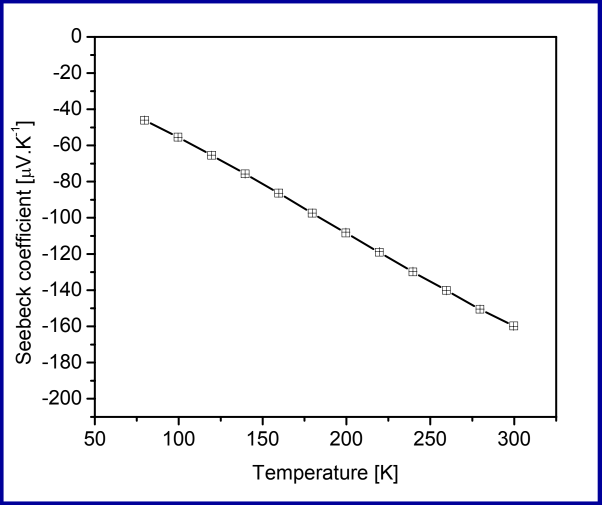
(T_s = 150°C, F = 4 J/cm^2)

	Resistivity [$\mu\Omega$.m]	Seebeck [μV.K^{-1}]	Power factor [μW.m^{-1}.K^{-2}]
PbTe/BaF_2	45	- 247	1355 (n=4.9x10^{17} cm^{-3})
20 (PbTe/Bi/BaF_2)	32	- 223	1554 (n=2.3x10^{18} cm^{-3})
PbTe/glass	14	- 156	1760 (n=2.0x10^{20}cm^{-3})
20(PbTe/Bi/glass)	8	- 118	1780

Thermal cycling of PbTe films and Bi/PbTe nanocomposites

The PbTe films do not withstand thermal cycling ...





…but the Bi/PbTe nanocomposites do !