Poudres nanocristallines de Bi_2Se_3 synthétisées à partir de H_2Se généré *in-situ* par voie électrochimique

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Outline

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Introduction

Bi_2Te_3 and $Bi_xSb_{2-x}Te_{3-y}Se_y$ alloys : Best bulk thermoelectric (TE) materials at room temperature since 1960 (ZT ~ 1 at 300 K)

BUT small progress with time

1990's: Low dimensionality effects improve the thermoelectrical properties

Theoretical studies: ZT_{1D} > ZT_{2D} > ZT_{3D} *Dresselhaus et al. Phys Rev B 1993*

Experimental work:

1D: $Bi_xSb_{2-x}Te_{3-y}Se_y$ nanowire arrays, BUT no evidence of ZT improvement yet
Stacey et al. JACS 2001 Nano Lett. 2005, Fleurial et al. Adv. Mater. 2005

2D: Bi_2Te_3/Sb_2Te_3 superlattice structures: ZT ~ 2.4 at 300 K, BUT high cost technology
Venkatasubramanian et al. Nature 2001

Nanostructured 3D materials (from nanocrystalline powders)

Low dimensionality effects

Conventional technology

Large-scale production

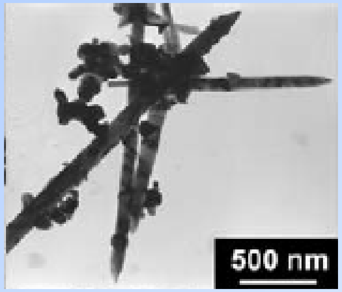
Recent promising news: $Bi_xSb_{2-x}Te_{3-y}$ ZT ~ 1.4 at 373 K, Bi_2Te_3/Sb_2Te_3 ZT ~ 1.5 at 440 K
Poudel et al. Nature 2008 — *Zhao et al. Appl. Phys. Lett. 2008*

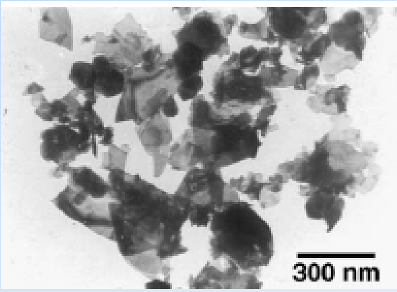
Introduction

Synthesis of Bi_2X_3 (X= Te, Se) nanocrystals

Solution techniques (low temp and cost):

- **Solvothermal** *Zhao et al. J. Alloys and Compounds 2005*
- **Sonochemistry** *Qiu et al. Inorg. Chem. Commun. 2004*
- **Micellar synthesis** *Foos et al. Nano Lett. 2001*
- **etc.**





Produced amounts are generally low (~ mg)

Considerable amounts of nanocrystalline (NC) powders are required for nanostructured 3D TE materials !

Bubbling gas precursors into the solution:

H_2X (X = Se, Te) as precursors: easily up-scalable
(~ grams of CdTe NC powders *Rogah et al. J. Phys. Chem. C 2007***)**

H_2X are toxic and present poor stability : storage problems!

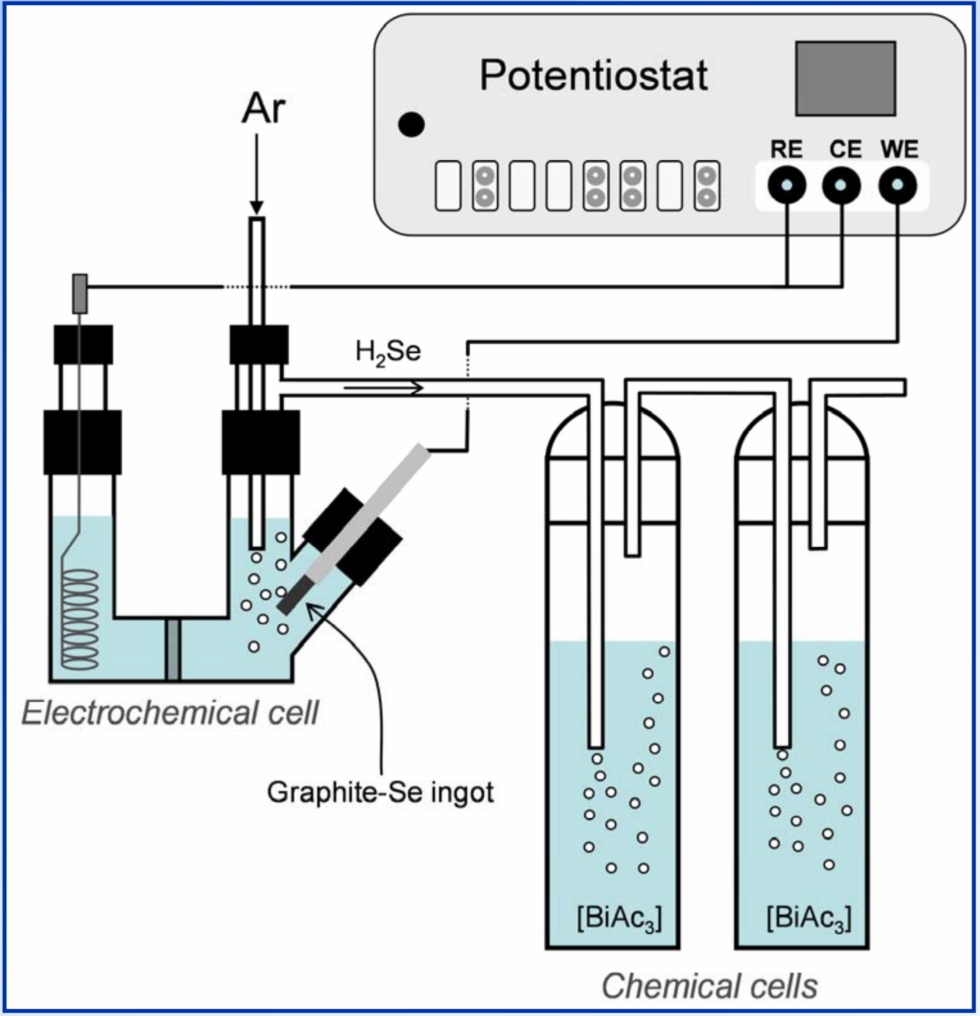
Our proposal: Electrochemical generation *in-situ*!

Synthesis

Experimental set-up

1. Electrochemical cell:
- Aqueous electrolyte ($[H_2SO_4]$ = 0.5 M)
- Cathode: graphite-Se ingot
- Anode: Platinum wire
- I = - 0.1 A

2. Chemical cells:
- Aqueous solution
  $[Bi(Ac)_3] = 1 \times 10^{-2}$ M
  $[HClO_4]$ = 1 – 10 M
  [X-100 Triton] = 5×10^{-4} M (surfactant)



1. Electrochemical generation of H_2Se

$$Se + 2e^- + 2H^+ \rightarrow H_2Se$$

Bastide et al. J. Electrochm. Soc. 2005

2. Transport of H_2Se (Ar: carrier gas)

3. Bi_2Se_3 formation (global reaction):

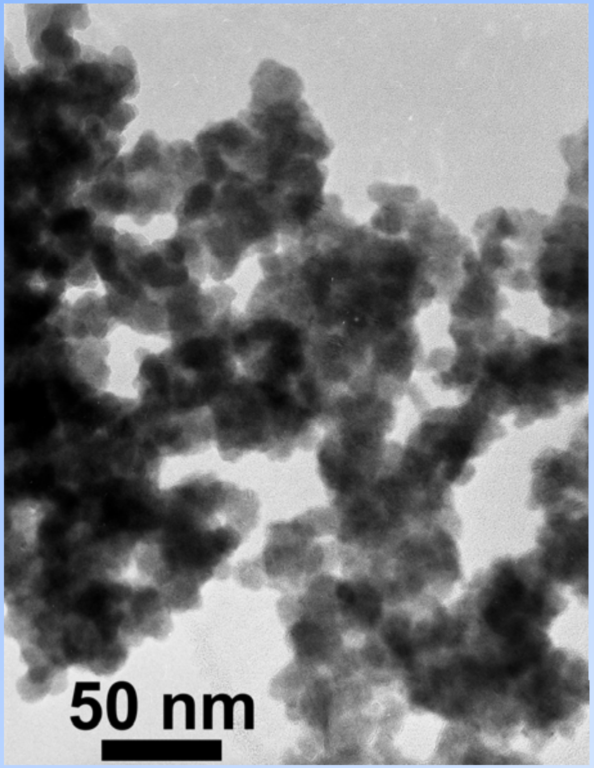
$$2Bi(Ac)_3 + 3H_2Se \rightarrow Bi_2Se_3 + 6HAc$$

4. Filtration: powder collection

Structural properties

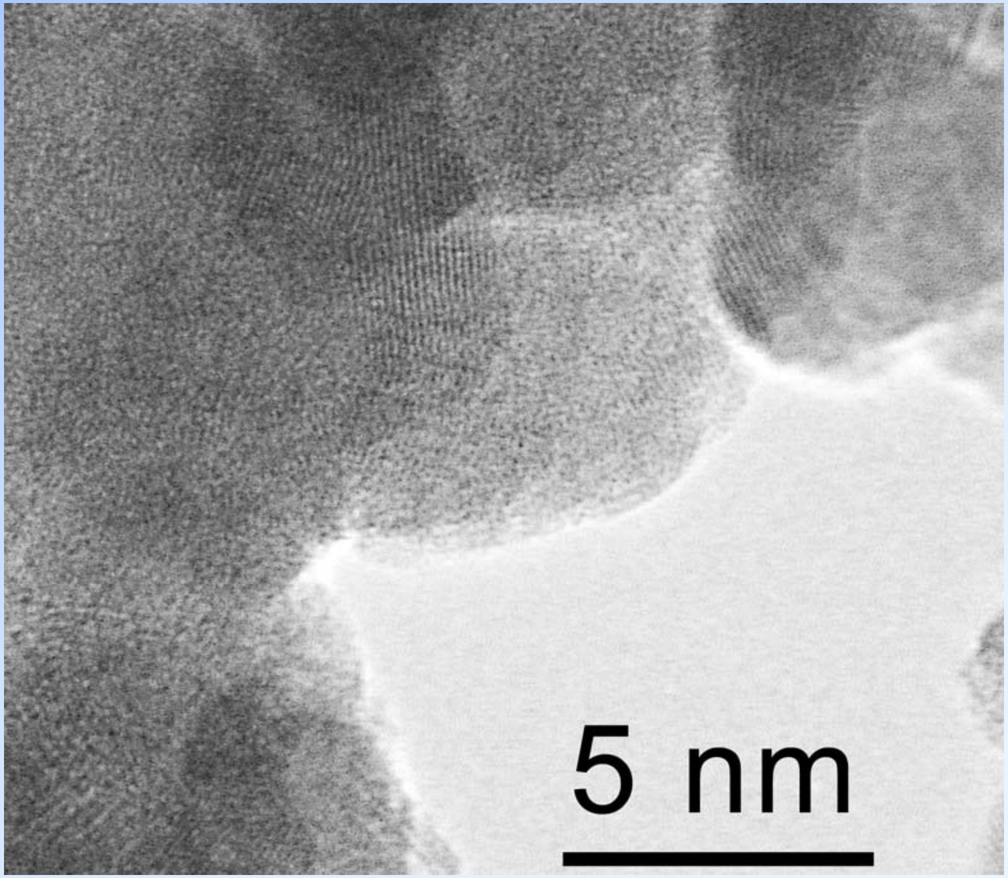
Transmission Electron Microscopy (TEM)
(before filtration)

Bright field image



Agglomerates > 10 nm

High resolution TEM



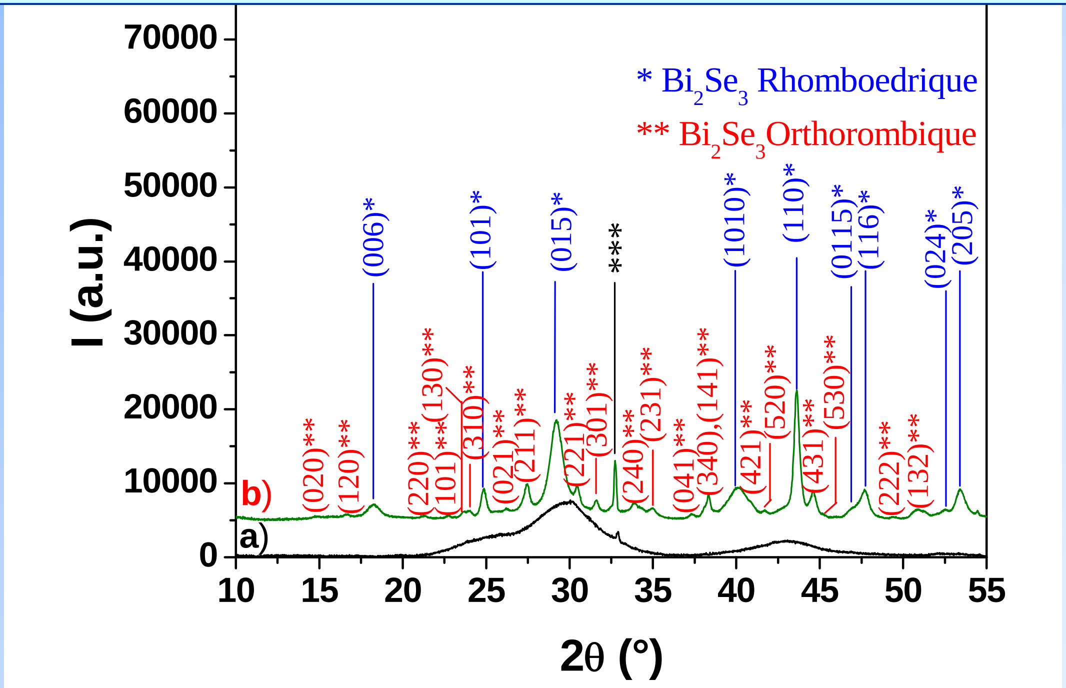
Crystalline domains ~ 5 nm

Structural properties

X ray Diffraction

Orthorhombic Bi_2Se_3: metastable

Under high pressure *Atabaeva et al. 1973* **or special ultrasonic treatment** *Qiu et al. JACS 2004*



As synthesized powders: Extremely broad diffraction peaks,

Ambiguous interpretation (small crystal size, several phases, ...?)

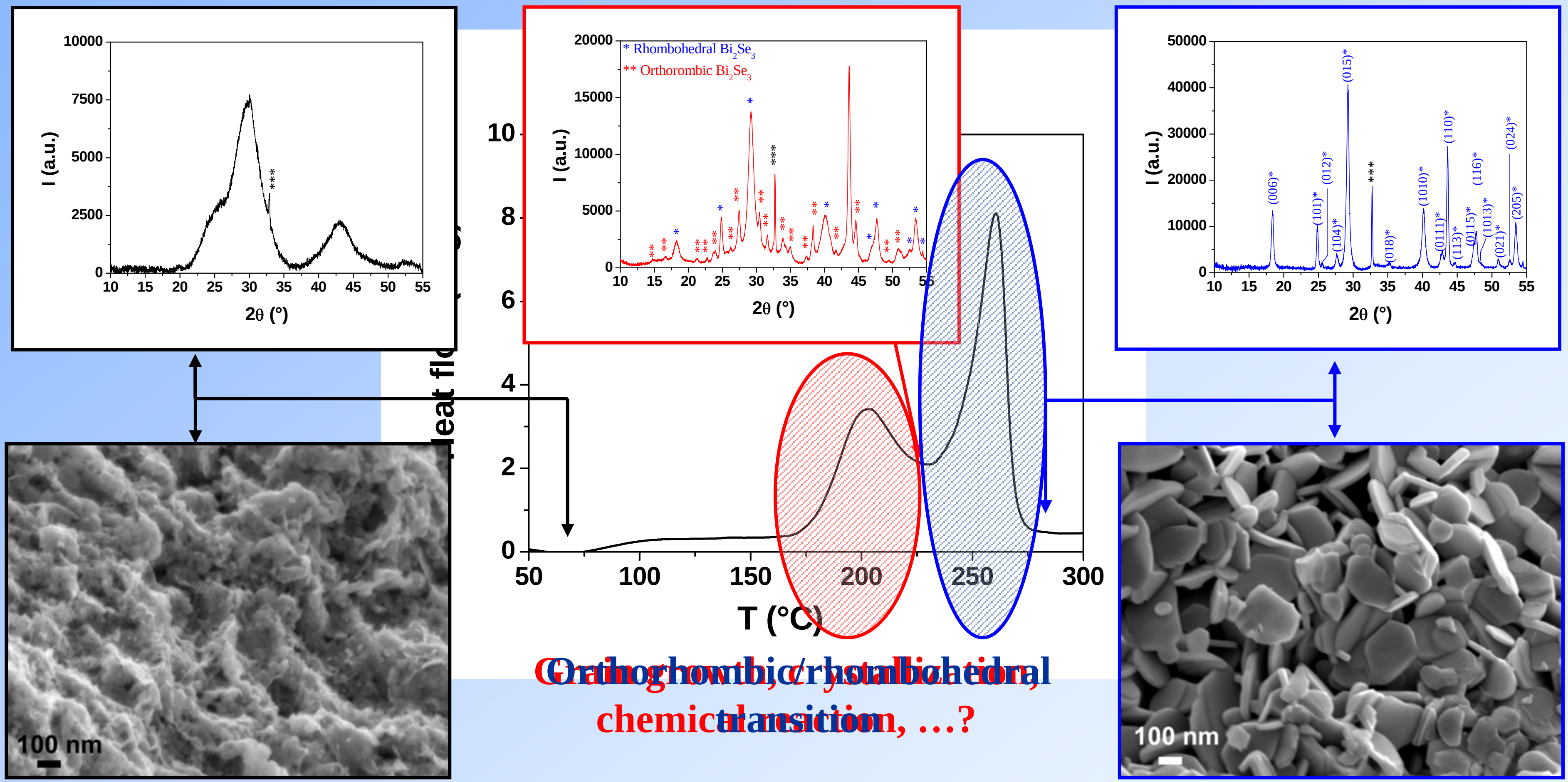
Annealing at low temperature (200°C): Two Bi_2Se_3 phases: rhombohedral and orthorhombic

No spurious phases

Structural properties

Stability range of orthorhombic Bi_2Se_3 in NC powders?

Differential Scanning Calorimetry (DSC)

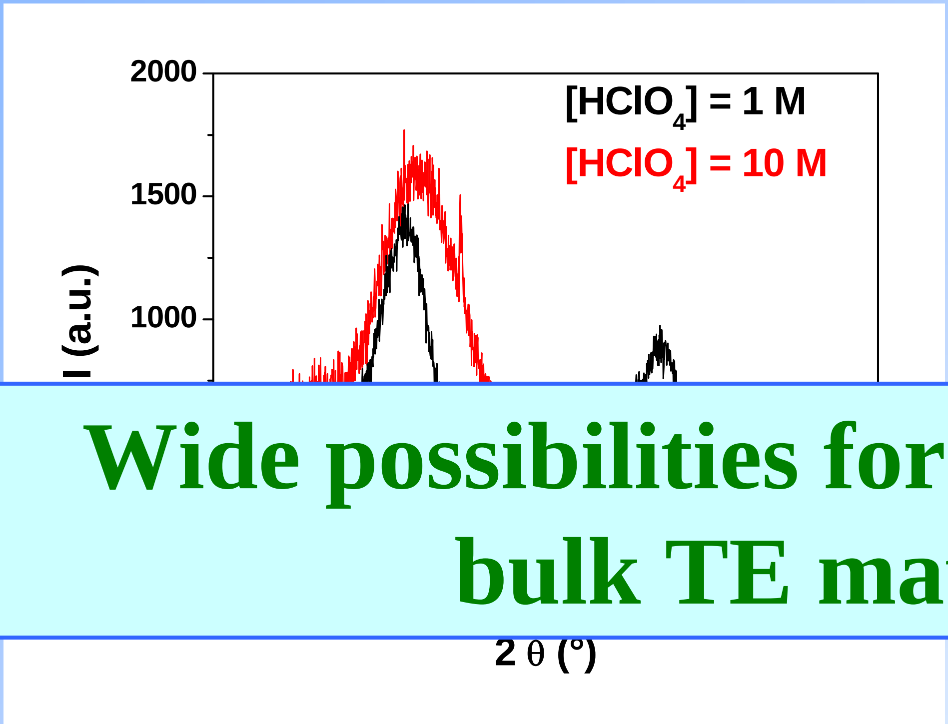


Orthorhombic Bi_2Se_3 stable up to T > 200 °C

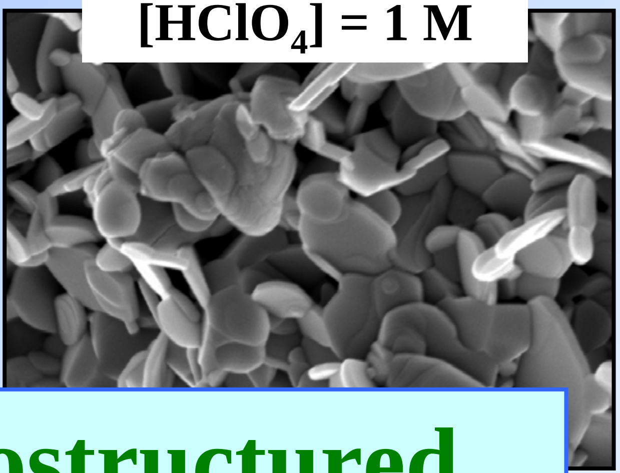
Structural properties

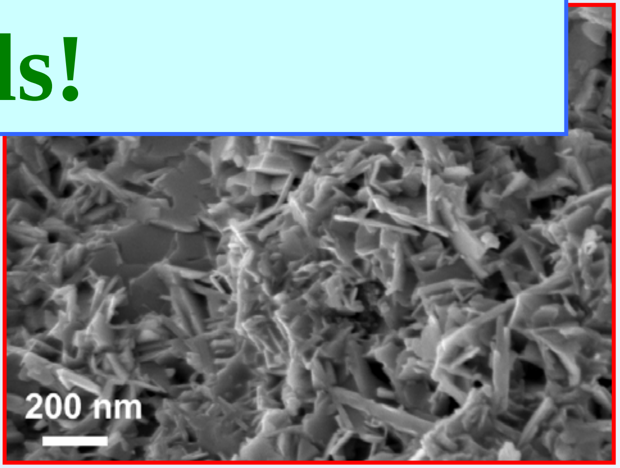
$[HClO_4]$ effects

As synthesized



Annealed at 400°C





Wide possibilities for nanostructured bulk TE materials!

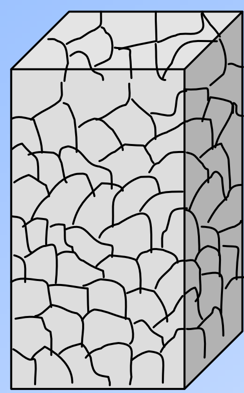
$[H^+]$ seems to be a major parameter:

$[HClO_4]$ ↗
- crystal size ↘
- Orth-Bi_2Se_3 / Rhomb-Bi_2Se_3 ↗

"Nanostructured bulk" Bi_2Se_3

Densification of Bi_2Se_3 NC powders

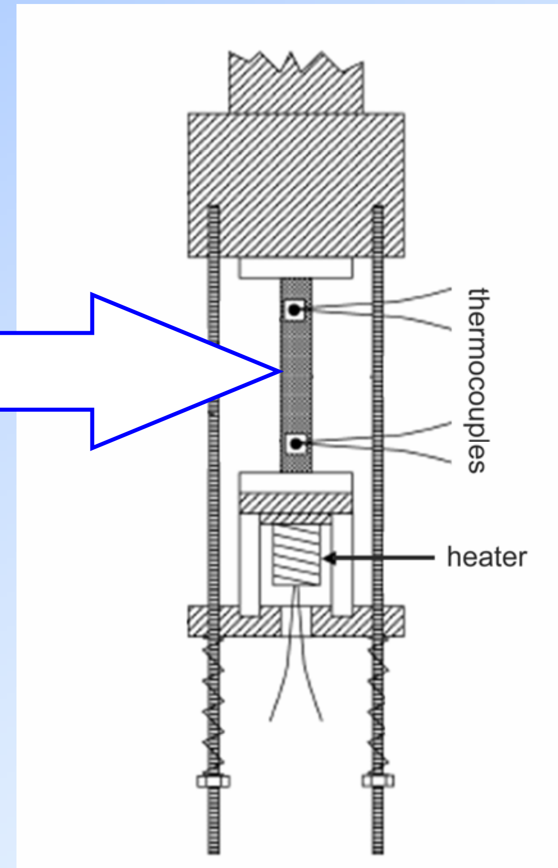
(pressing at 300 °C under ~ 400 MPa)



10mm×2mm×1mm
nanostructured bulk samples

Rhombohedral Bi_2Se_3

Thermopower measurements



Preliminary results: S = - 125 µV/K at room temperature

Conclusions and future work

- Innovative route (low cost and low temperature) to obtain considerable amounts (> 200 mg/synthesis) of powders constituted of Bi_2Se_3 nanocrystals (~ 5 nm)
- Synthesis of orthorombic Bi_2Se_3 nanocrystals (stable up to T > 200 °C, higher than working temperature of Bi_2Te_3 based TE devices).
- "Nanostructured bulk" Bi_2Se_3 with Seebeck coefficient ~ -125 µV/K.
- Optimization of the densification process (Spark Plasma Sintering)
- Study of thermoelectric properties of orthorhombic Bi_2Se_3
- "Nanostructured bulk" with rhombohedral/orthorhombic interfaces to reduce the thermal conductivity

Merci pour votre attention

Triton X-100 = t-Oct-C_6H_4-$(OCH_2CH_2)_{9-10}OH$