

SYNTHESIS AND CHARACTERIZATION OF $\text{Cu}_{12-x-y}\text{Zn}_x\text{Fe}_y\text{Sb}_4\text{S}_{13-z}$ TETRAHEDRITES

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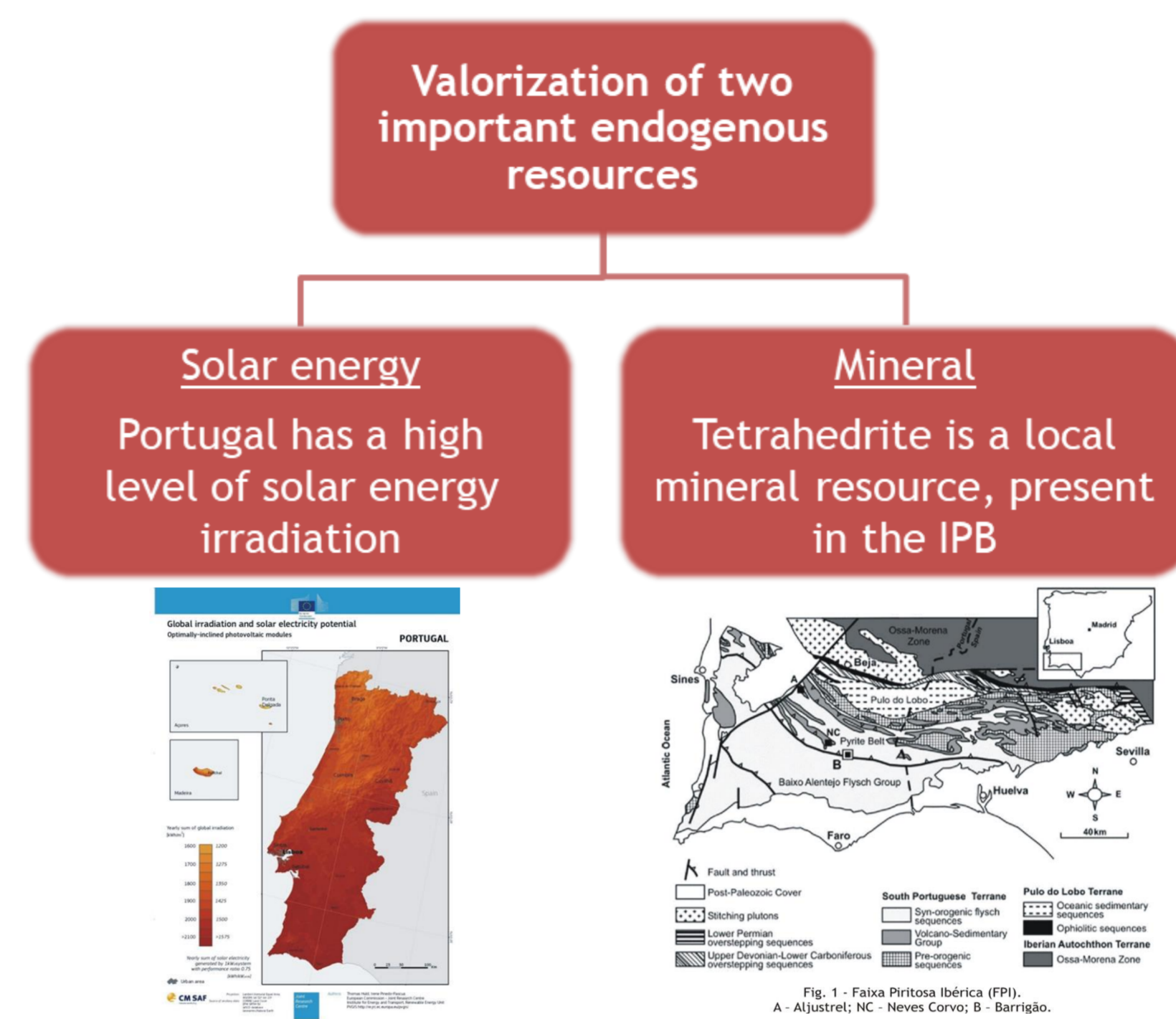
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Background

LocalEnergy project focuses on the valorization of endogenous resources (solar and mineral) through the development of energy-harvesting applications based on the tetrahedrite mineral, which offers a high exploitation potential. Naturally occurring tetrahedrite series consists of earth-abundant and relatively non-toxic elements and can be generically expressed as $\text{Cu}_6[\text{Cu}_4(\text{Fe,Zn})_2]\text{Sb}_4\text{S}_{13}$. Besides that, tetrahedrites show p-type semiconductor material behavior with high Seebeck coefficient, a complex cubic crystal structure and extremely low thermal conductivities at moderate temperatures, reaching $zT \sim 0.7$ around 700K after adequate doping. Owing to these properties they are considered as a suitable and promising thermoelectric material.

LocalEnergy characteristics



Develop materials and systems for energy-harvesting applications

Thermoelectric materials

New absorbers materials for TFSC

Tetrahedrite-based materials ($\text{Cu}_{12-x}\text{M}_x\text{Sb}_4\text{S}_{13}$)

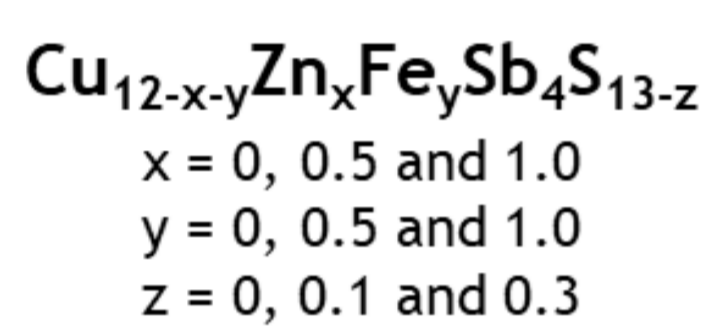
Natural

Synthetic

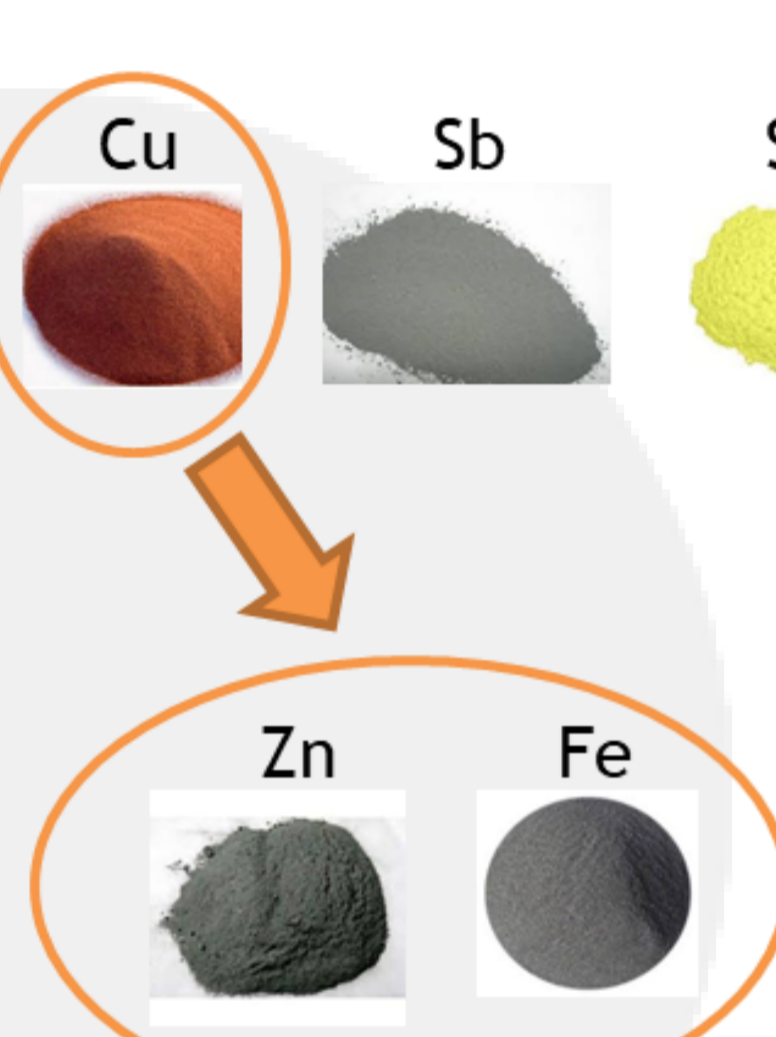
Synthetic

Powder sintering of synthetic tetrahedrites

Target composition



Raw materials



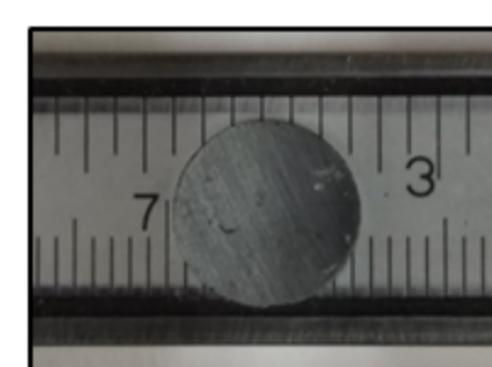
Mixed and sealed inside glove box

Mechanical alloying

380 rpm // 2 h
BPR 20:1
stainless steel jars and balls (15 mm)



Hot-pressing
515 °C // 1h30m
~ 60 MPa
0.6 g



Objectives of the presente work

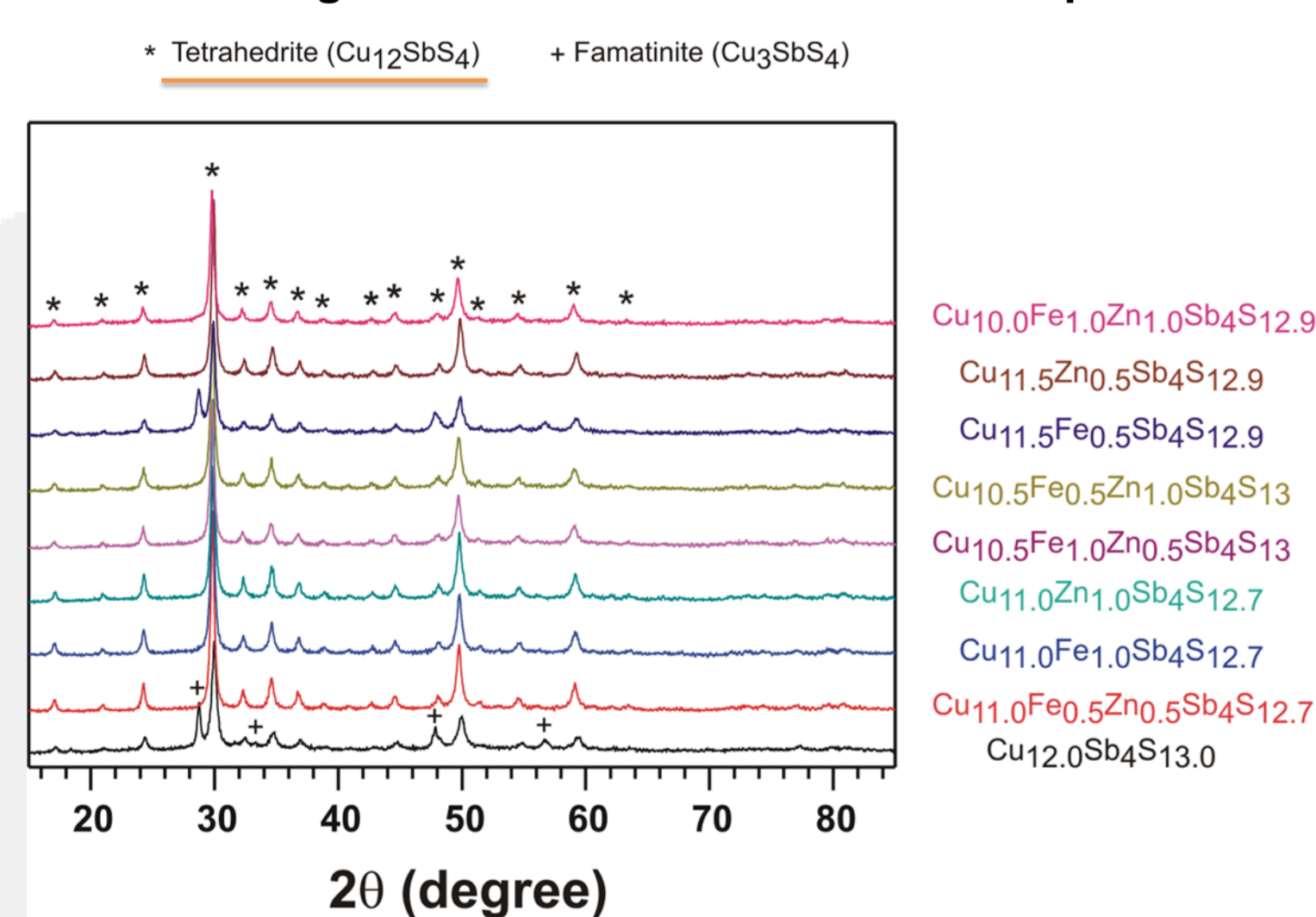
Develop a fast-solid-state synthesis method based on powder sintering for producing synthetic tetrahedrites.

Conclusions

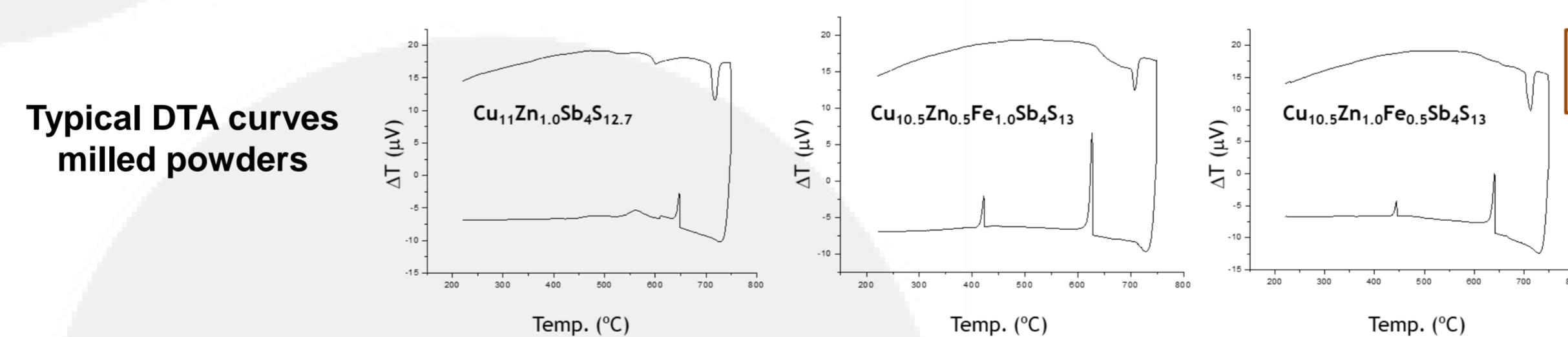
- Direct synthesis of single-phase tetrahedrite materials achieved after a short mechanically alloying step (2 h).
- Fully dense bulk tetrahedrite materials were obtained by hot-pressing.
- Reduction in the overall processing time when compared with that of conventional synthesis methods.

Results

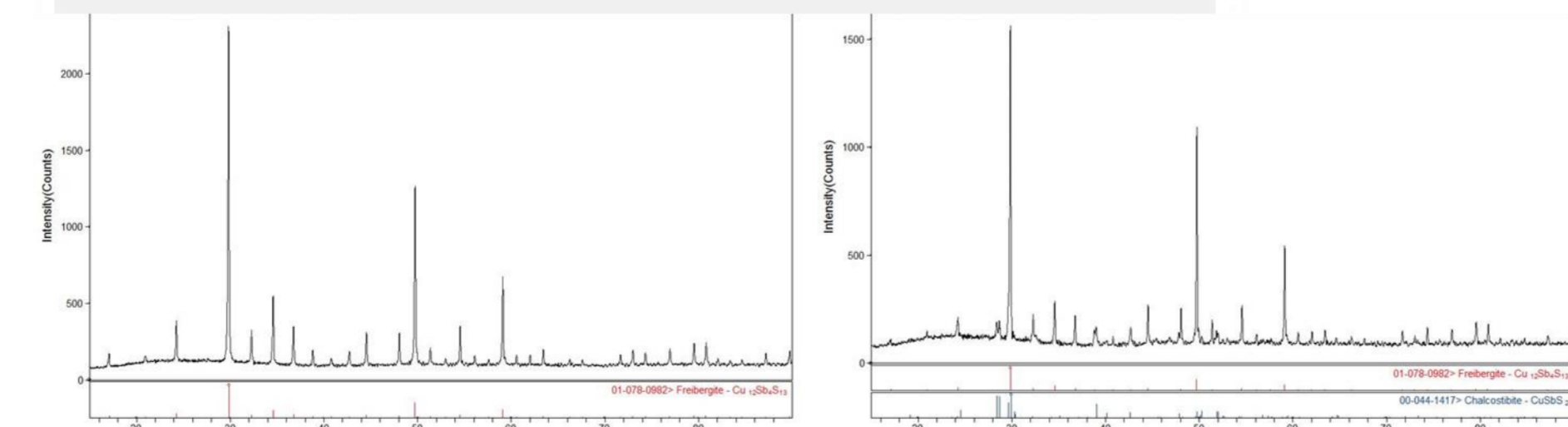
Typical XRD patterns of the milled powders showing the formation of the tetrahedrite phase



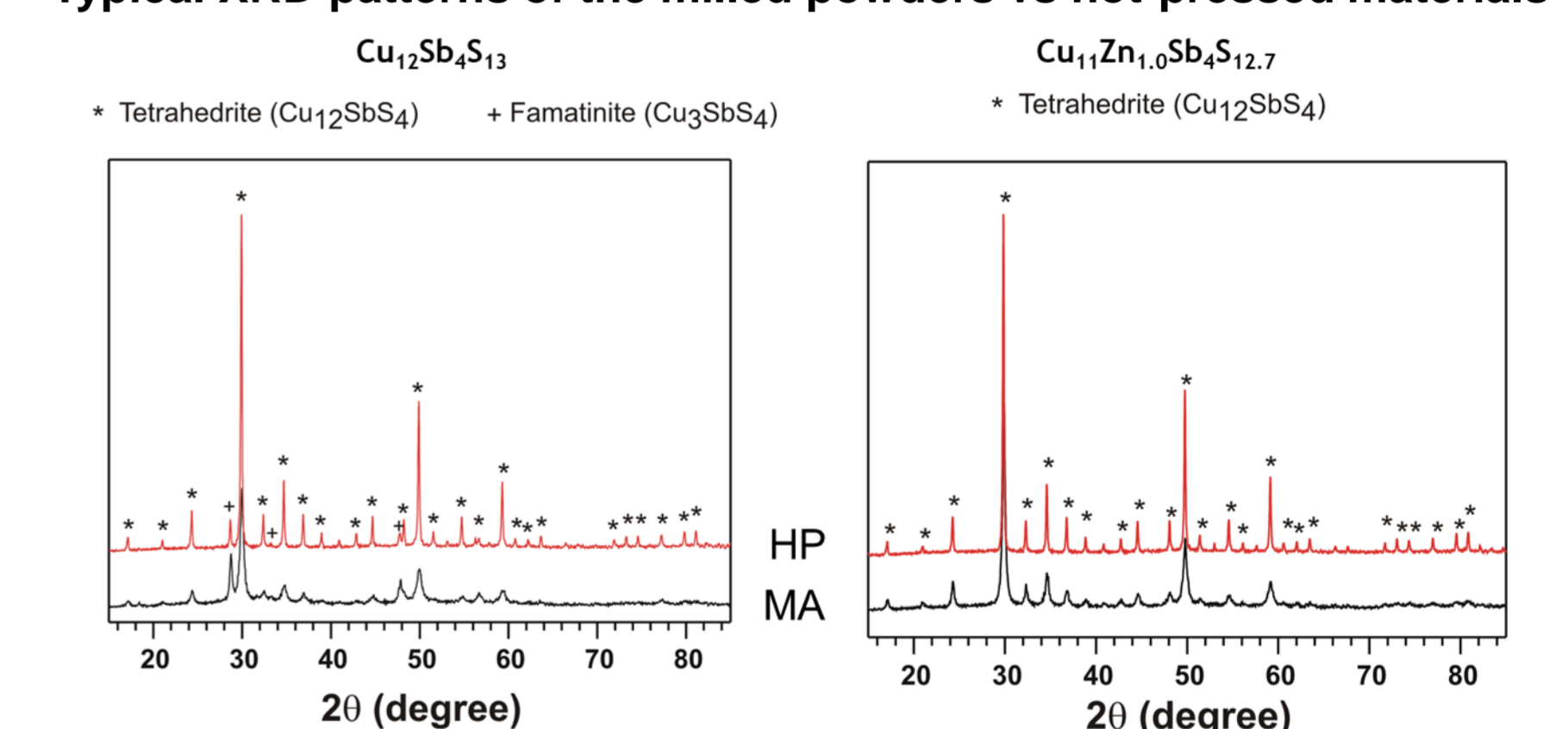
Typical DTA curves milled powders



XRD patterns obtained after heating the milled powders at 500 °C and 700 °C



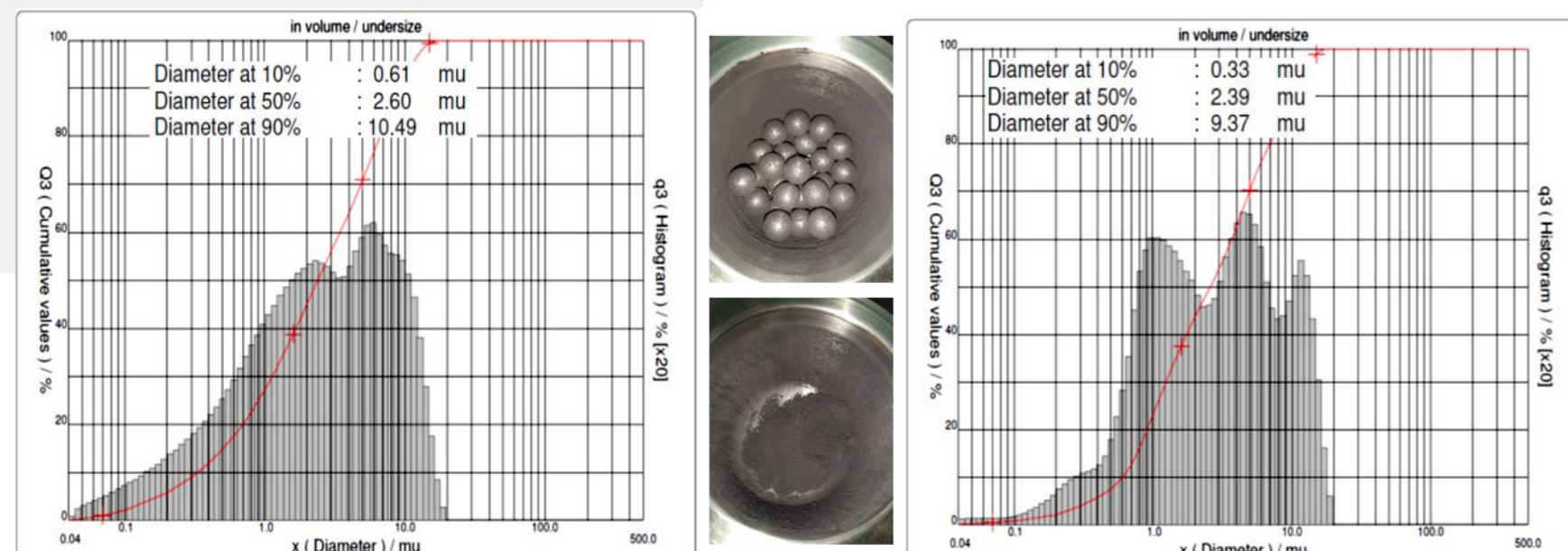
Typical XRD patterns of the milled powders vs hot-pressed materials



Typical density (g/cm^3) obtained for the hot-pressed materials

Composition	Density (g/cm^3)
$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	4.34
$\text{Cu}_{11}\text{Zn}_{0.5}\text{Fe}_{0.5}\text{Sb}_4\text{S}_{12.7}$	4.89
$\text{Cu}_{11}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{12.7}$	5.01
$\text{Cu}_{11}\text{Zn}_{1.0}\text{Sb}_4\text{S}_{12.7}$	4.97
$\text{Cu}_{10.5}\text{Zn}_{0.5}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$	4.88
$\text{Cu}_{10.5}\text{Zn}_{1.0}\text{Fe}_{0.5}\text{Sb}_4\text{S}_{13}$	4.91
$\text{Cu}_{11.5}\text{Fe}_{0.5}\text{Sb}_4\text{S}_{12.9}$	4.80
$\text{Cu}_{11.5}\text{Zn}_{0.5}\text{Sb}_4\text{S}_{12.9}$	4.98
$\text{Cu}_{10.0}\text{Zn}_{1.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{12.9}$	4.26
Average	4.91 - 5.02 (g/cm^3)

Typical particle size distribution of the milled powders



Typical BSE images of the (a) milled powders and (b) hot-pressed materials

