Structural and optical characterization of mechanochemically synthesized $CuSbS_2$

Luís Esperto[1], Isabel Figueira[1], João Mascarenhas[1], Teresa Pena Silva[2], José Brito Correia[1] and Filipe Neves[1]

[1] LNEG, Laboratório Nacional de Energia e Geologia, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal
[2] LNEG, Laboratório Nacional de Energia e Geologia, Estrada da Portela, Bairro do Zambujal – Alfragide, Apartado 7586, 2610-999 Amadora, Portugal

filipe.neves@lneg.pt

This work is funded by national funds through the FCT – Fundação para a Ciência e a Tecnologia, I.P., under the project PTDC/EAM-PEC/29905/2017

Outline

Topic introduction

- Photovoltaic technologies (PV) - Thin film solar cells
- Earth-abundant and eco-friendly absorber materials
- Objectives

Experimental details

Results

Final remarks

Topic introduction

PV Technologies

Materials science is key enabler for green transition

Green transition

Materials science-based solutions are vital for designing improved materials and devices

Use of a broad mixture of renewable energy sources.

Photovoltaic (PV) materials

Active research topic in the field of materials for energy applications

Despite the progress that has been achieved in materials and production processes, PV materials current research is still facing many challenges concerning, e.g., materials availability, environmental issues and processability to achieve low cost, efficiency and durability.

Topic introduction

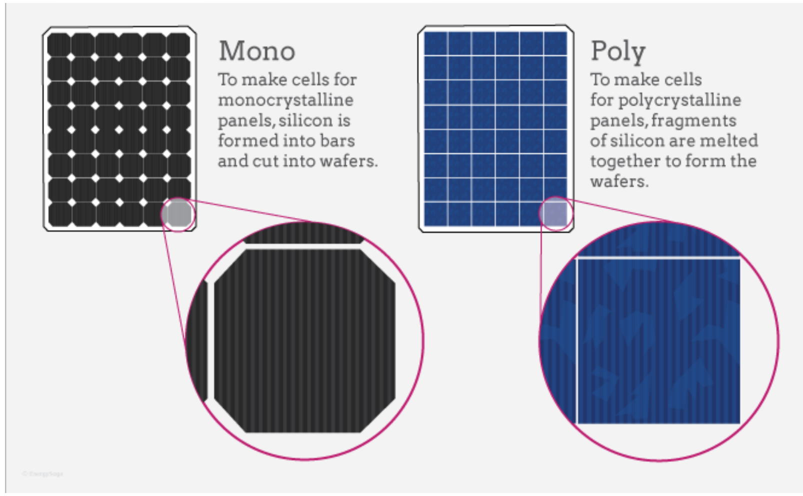
PV technologies

Wafer-based
1^{st} generation PV

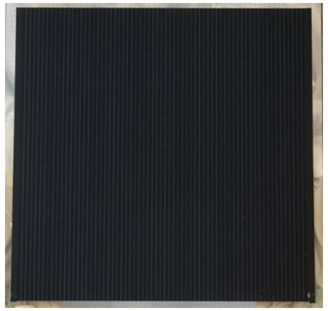
- Crystalline silicon (c-Si)
  - Mono-crystalline Si
  - Multi-crystalline Si
- GaAs & III-V single junction

Thin film cells

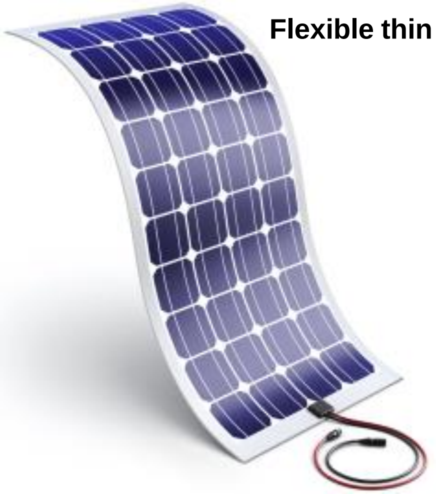
- Conventional thin film – 2^{nd} generation PV
  - Amorphous Si (a-Si)
  - Cadmium telluride (CdTe)
  - Copper indium gallium diselenide (CIGS)
- Emerging thin film – 3^{rd} generation PV
  - Copper zinc tin sulfide (CZTS)
  - Dye sensitized solar cell
  - Perovskite
  - Organic Photovoltaic (OPV)
  - Quantum dot (QD PV)



Thin film module



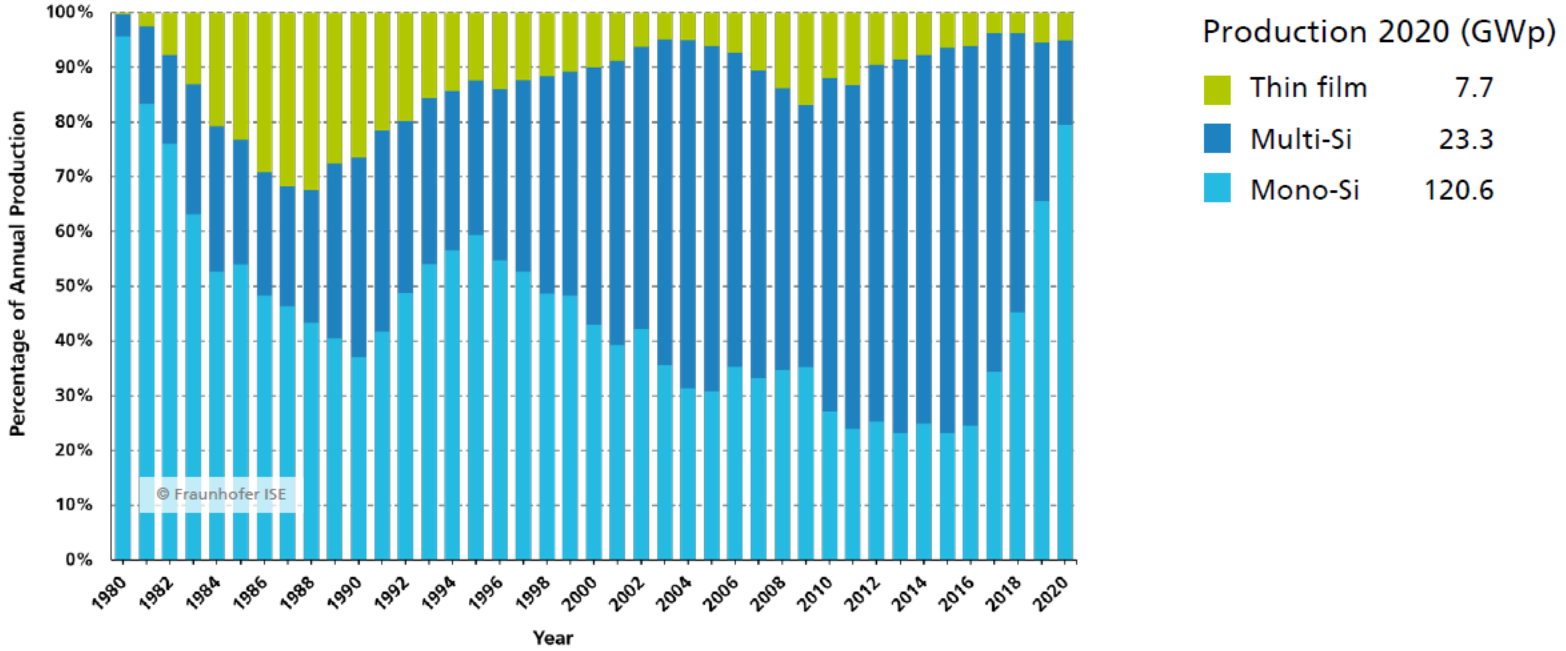
Flexible thin film



HR EXCELLENCE IN RESEARCH

PV Technologies

PV Production by Technology
Percentage of Global Annual Production

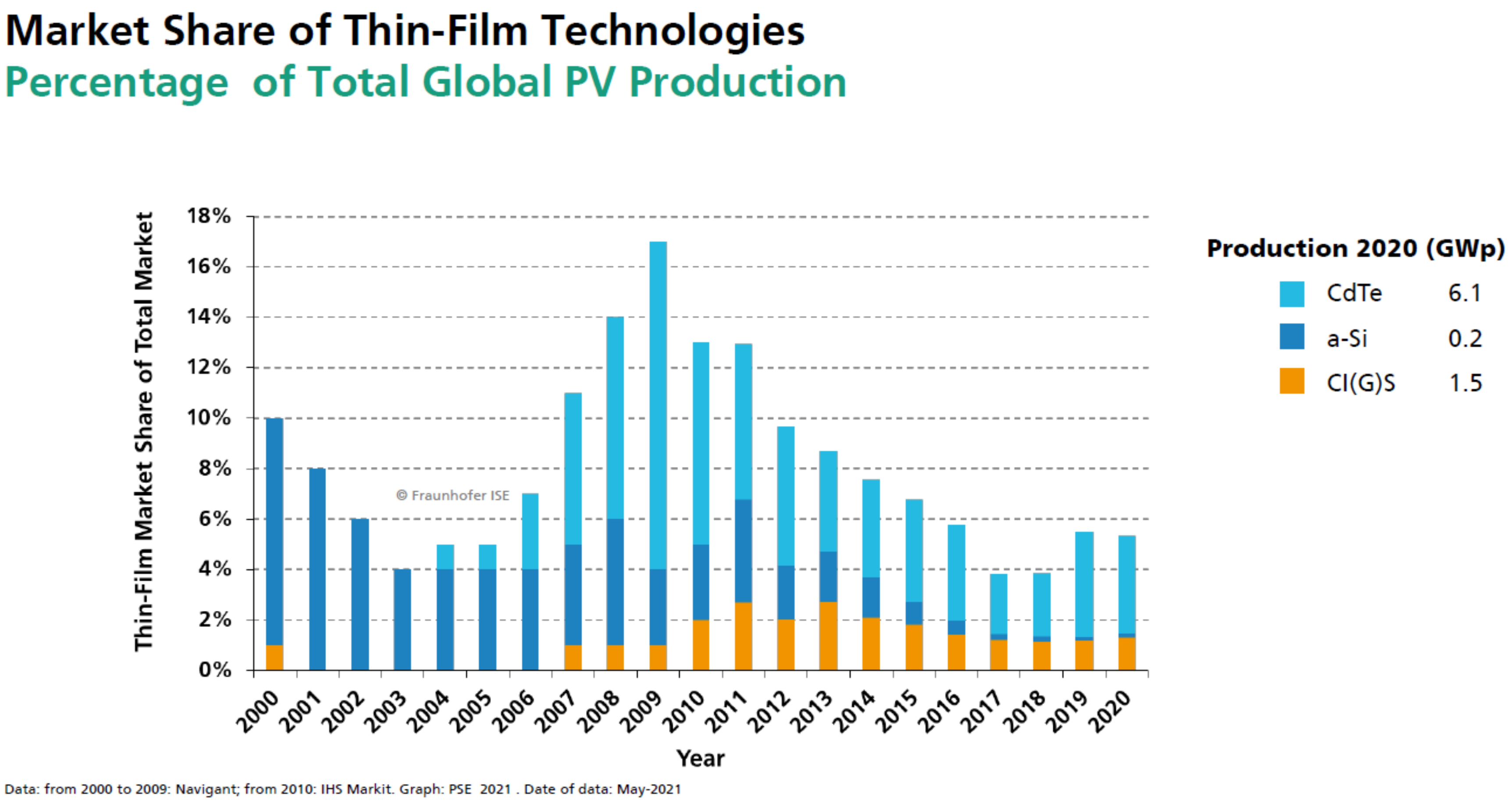


Data: from 2000 to 2009: Navigant; from 2010: IHS Markit. Graph: PSE 2021. Date of data: May-2021

©Fraunhofer ISE: Photovoltaics Report, updated: 24 February 2022
Fraunhofer Institute for Solar Energy Systems, ISE

Topic introduction

Thin film solar cells



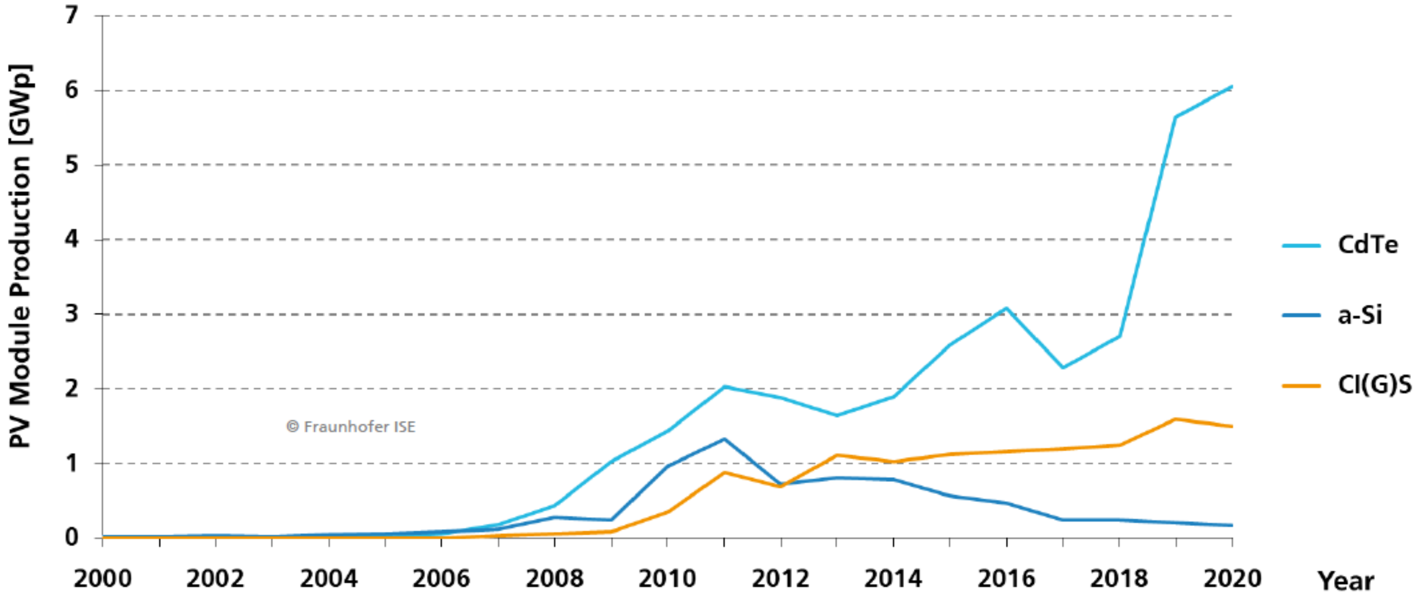
©Fraunhofer ISE: Photovoltaics Report, updated: 24 February 2022
Fraunhofer Institute for Solar Energy Systems, ISE

Topic introduction

Thin film solar cells

Thin-Film Technologies

Annual Global PV Module Production



Data: from 2000 to 2009: Navigant; from 2010: IHS Markit. Graph: PSE 2021 . Date of data: May-2021

HR EXCELLENCE IN RESEARCH

Topic introduction

Thin film solar cells

Main limitations

- **a-Si**: low efficiency
- **CdTe, CIGS**: scarcity (In, Ga, Te) and toxicity (Cd)
- **CZTS**: compositional heterogeneities, manufacturing process
- **Perovskite**: thermal degradation (lack of thermal stability) and toxicity (Pb)

These considerations have led to increased interest in emerging light-absorber materials

- containing modestly earth-abundant, and relatively non-toxic elements

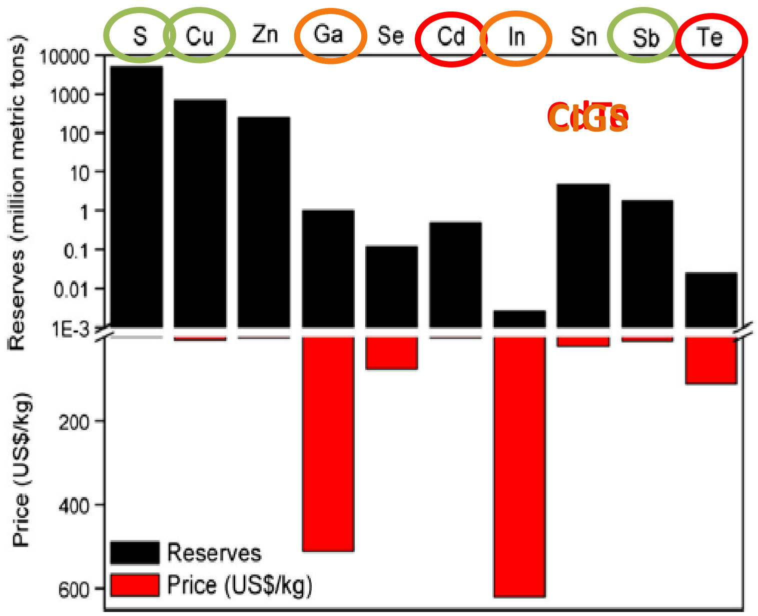
Earth-abundant and eco-friendly absorber materials

One class of such non-toxic earth-abundant less-complex and low-dimensional absorbers is **ternary copper chalcogenides**, such as **$CuSbS_2$ (CAS) chalcostibite**

CAS main characteristics

+	−
p-type electrical conductivity	Low efficiency (~3%)
Tunable optical bandgap (1.4-1.5 eV)	Synthesis: various physical and chemical methods have been reported - most of them involve post-deposition treatments of sulfurization
Strong optical absorption coefficient > 10^5 cm^{-1}	
Orthorhombic layered crystal structure	

Comparison on elemental abundance and price



Krishnan, B., Shaji, S. & Ernesto Ornelas, R. J Mater Sci: Mater Electron (2015) 26: 4770.

Objectives

To produce chalcostibite ($CuSbS_2$) materials by mechanochemical synthesis (MCS)

- Unique characteristics: solid-state synthesis, scalable and environmentally friendly technology

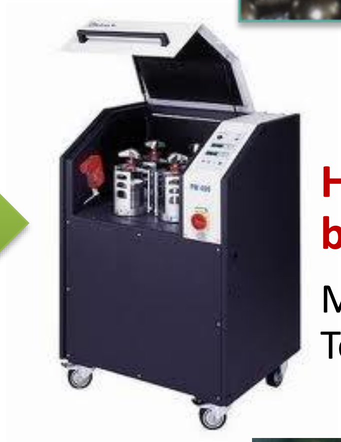
To characterize the produced $CuSbS_2$ materials in terms of their structural and optical properties – PV applications

Experimental details

Chalcostibite ($CuSbS_2$) powders obtained by mechanochemical synthesis (MCS)

X40Cr13 stainless steel jars (250 mL) and balls (15 mm), without any additional fluid medium

The jars were sealed, evacuated, and back filled with Ar gas



High-energy planetary ball mill PM 400/Retsch;

Milling speed: 340 rpm
Total time: 2 h

Ball-to-powder ratio of 20:1

Milling periods of 10 min were alternated with 5 min periods of rest

Thermal heat treatment

350 ºC for 24 h
Vacuum (10^{-2} mbar)

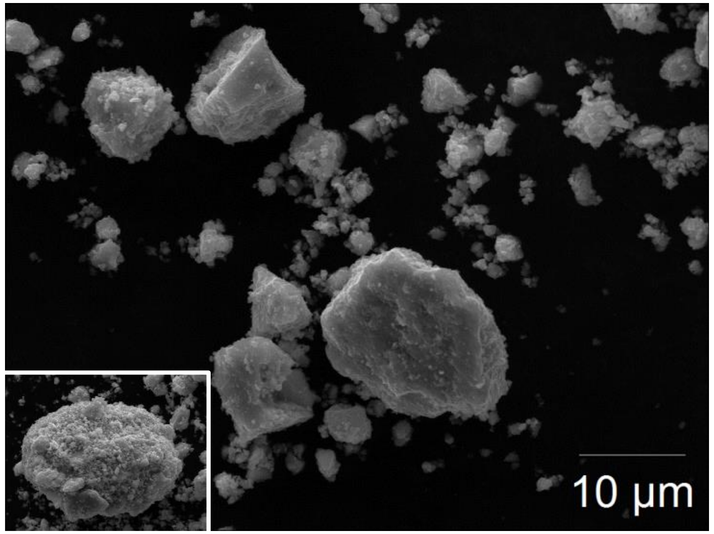
Experimental details

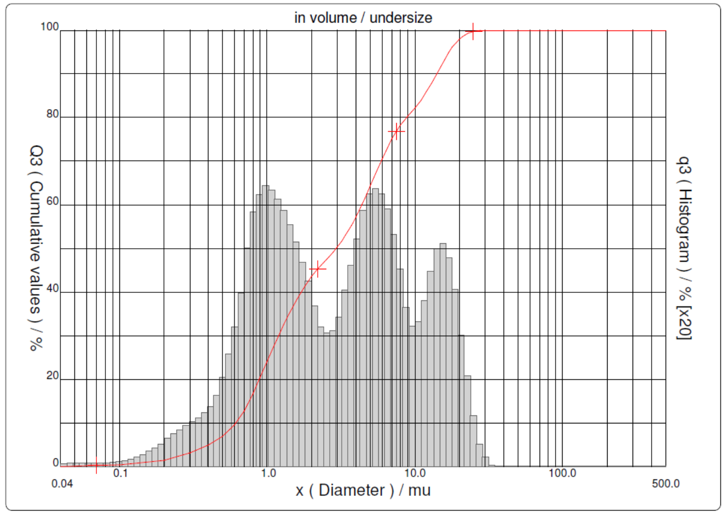
Characterization techniques

- X-ray diffraction (Cu-K_{α} radiation) (XRD) // Rietveld refinement using Diffrac.TOPAS (Bruker AXS)
- Field emission scanning microscopy (FE-SEM) with backscattered electron detector (BSE)
- Laser scattering (for particle size distribution evaluation)
- Differential thermal analysis (DTA)
- UV-VIS-NIR spectroscopy (diffuse reflectance mode)

Results

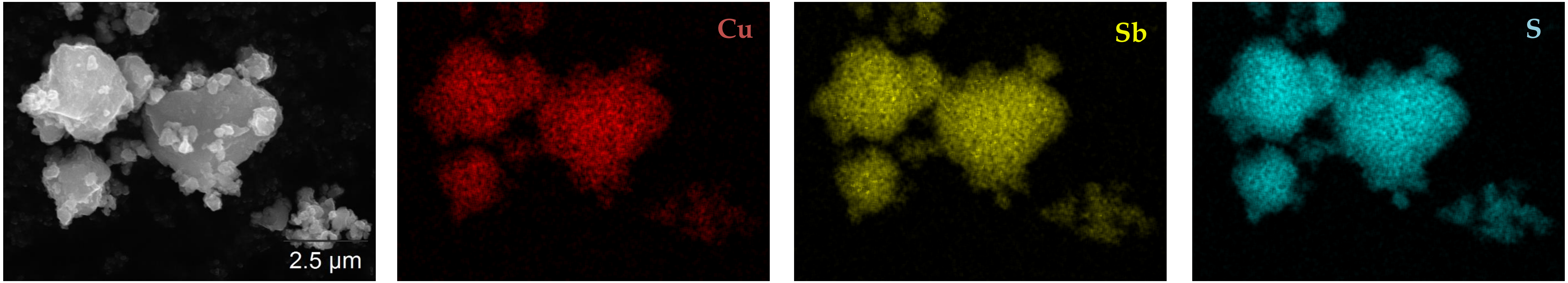
Morphology and particle size distribution after MCS





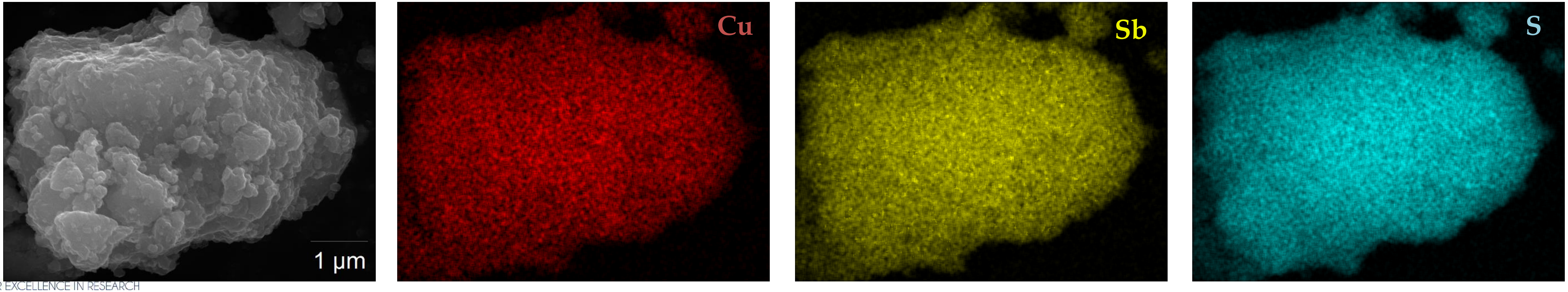
- Morphology is quite irregular, generically presenting three types of fractions: one at the submicrometric scale and the other two of the order of a few µm to tens of µm.
- The submicron fraction tends to aggregate in micron-sized agglomerates.
- These observations were corroborated by the values of the characteristic dimensions of the particles and by the granulometric distribution:
  - D10: 0.42-0.61 µm
  - D50: 2.93-3.10 µm
  - D90: 14.09-14.29 µm
  - The frequency distribution curve (q3, histogram) reveals a multimodal distribution.

EDS elemental mapping for the 2 h MCS $CuSbS_2$ powders

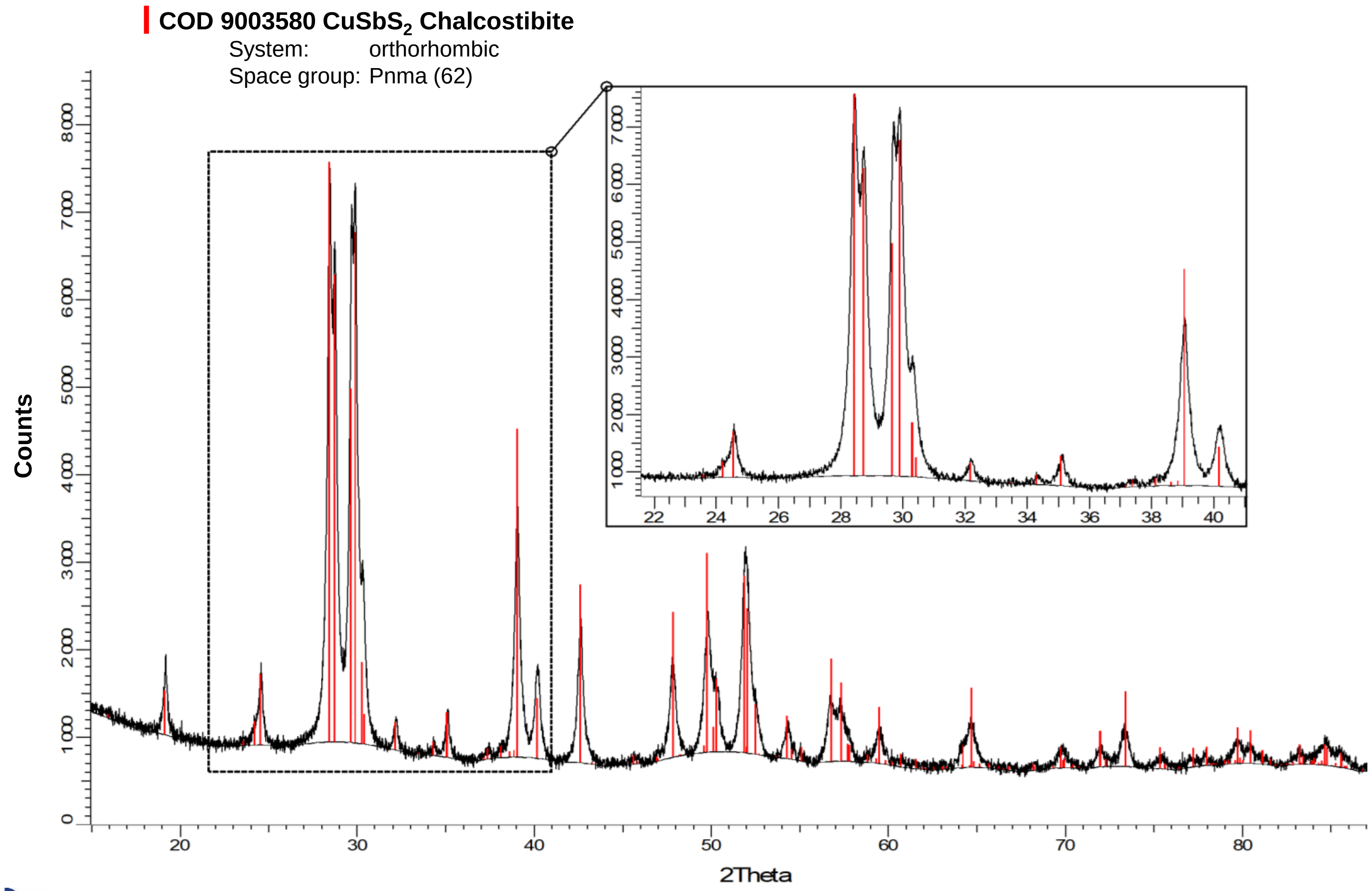


The chemical mappings revealed that the Cu, Sb and S elements are evenly distributed throughout the analyzed particles.

Considering the starting elemental powder mixture, the uniform distribution of Cu, Sb and S after the MCS process is extremely relevant.



XRD pattern for the 2 h MCS $CuSbS_2$ powders

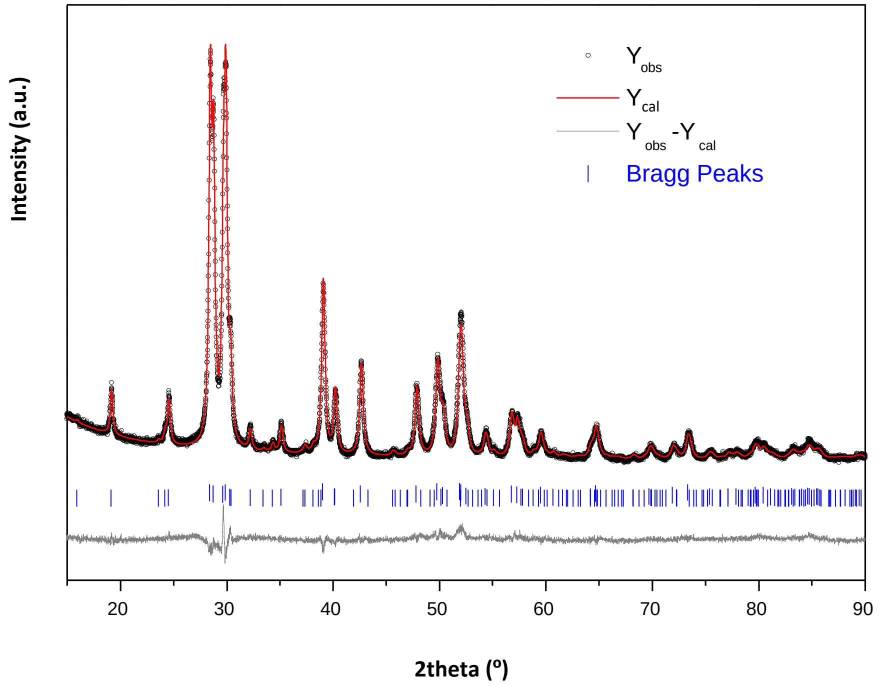


- All the main reflections from the XRD pattern were assigned to the orthorhombic structure with the space group Pnma (62). There was a successful and fast conversion of the pristine elements into the chalcostibite phase.
- No secondary phases were detected.
- The broadening and low intensity of the Bragg peaks is mainly a consequence of the MCS process which causes low crystallite size and high lattice strain.

Results

Typical Rietveld analysis outputs for the 2 h MCS $CuSbS_2$ powders

The orthorhombic structure with the space group Pnma (62)
(COD 9003580) was used as structural model in the refinement



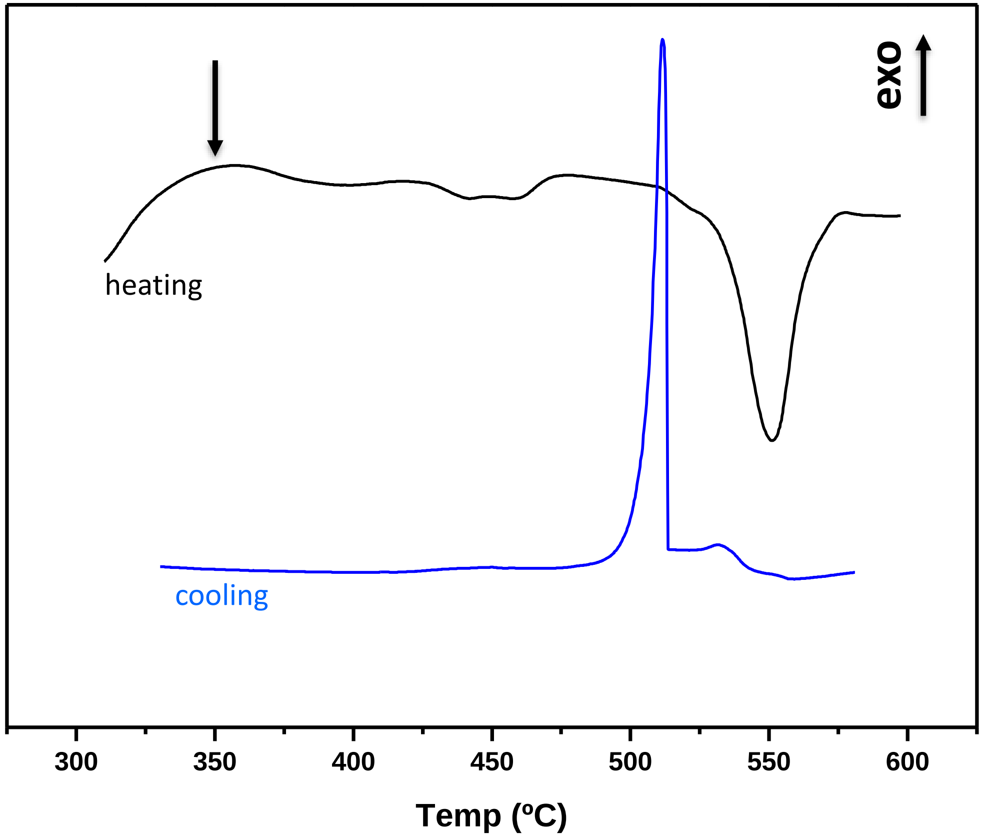
R_{exp}	R_{wp}
2.56	3.80

Cryst. Size (nm)	26	
Lattice parameters		*standard values*
a (Å)	6.02	*6.018*
b (Å)	3.80	*3.7958*
c (Å)	14.50	*14.495*

The values obtained for the R factors (R_{exp} (expected R factor) and R_{wp} (weighted profile R factor) ensure the good level of the refinement

Results

Differential thermal analysis for the 2 h MCS $CuSbS_2$ powders



- For $CuSbS_2$, the onset of thermal decomposition (to $Cu_{12}Sb_4S_{13}$, Sb_2S_3, and Sb_4) has been recorded for temperatures > 400 °C

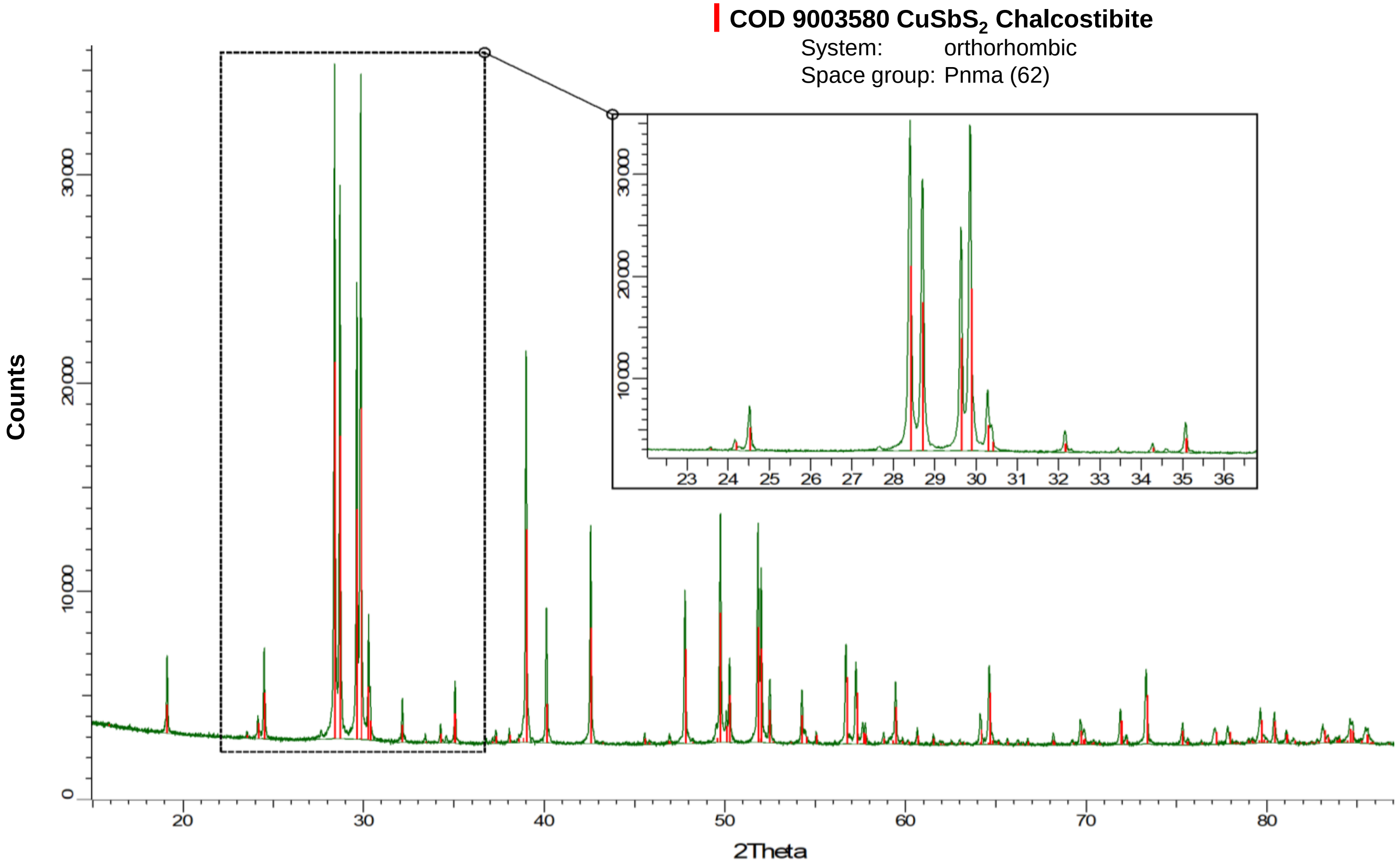
Peccerillo, E., Durose, K., MRS Energy & Sustainability 5, 9 (2018) https://doi.org/10.1557/mre.2018.10

- Melting temperature of ~552 ^{o}C

Welch A.W., Zawadzki P.P., Lany S., Wolden C.A., and Zakutayev A., Sol. Energy Mater. Sol. Cells 132, 499–506 (2015) http://dx.doi.org/10.1016/j.solmat.2014.09.041

Results

XRD pattern for the 2 h MCS $CuSbS_2$ powders heat treated at 350 ºC/ 24 h



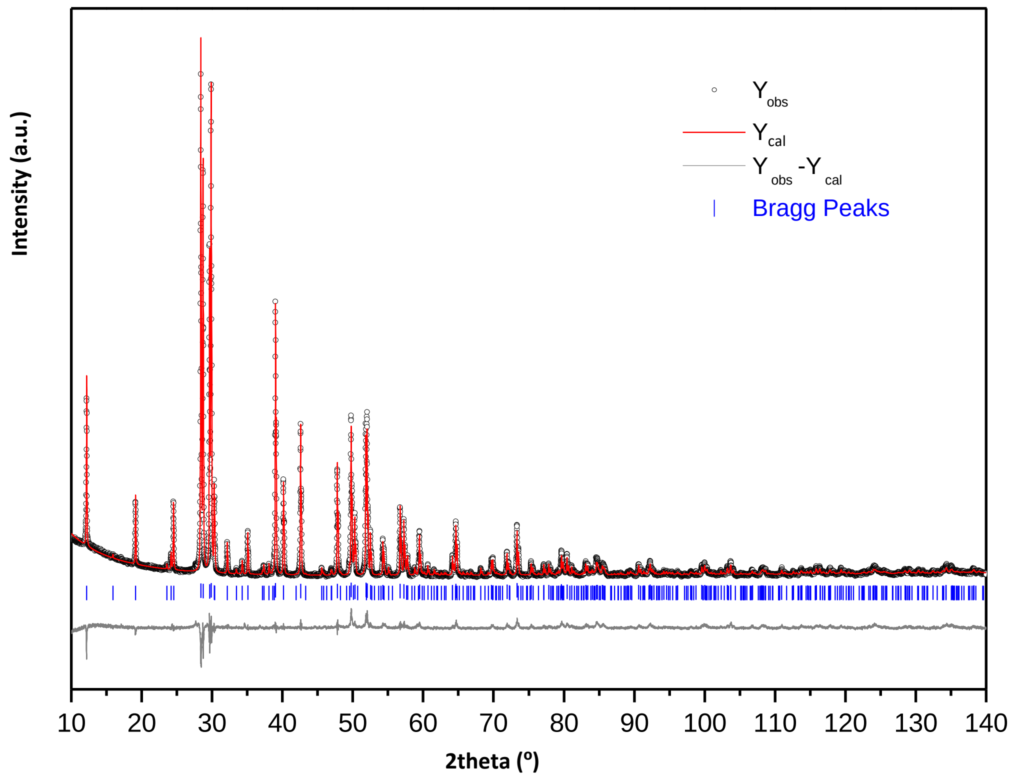
- All the main reflections from the XRD pattern were assigned to the orthorhombic structure with the space group Pnma (62).

- The Bragg peaks are sharper and better defined than those of the MCS powders. This can be attributed to the increase of the crystallite size and reduction of internal strains.

Results

Typical Rietveld analysis outputs for the 2 h MCS $CuSbS_2$ powders heat treated at 350 ºC/ 24 h

The orthorhombic structure with the space group Pnma (62)
(COD 9003580) was used as structural model in the refinement



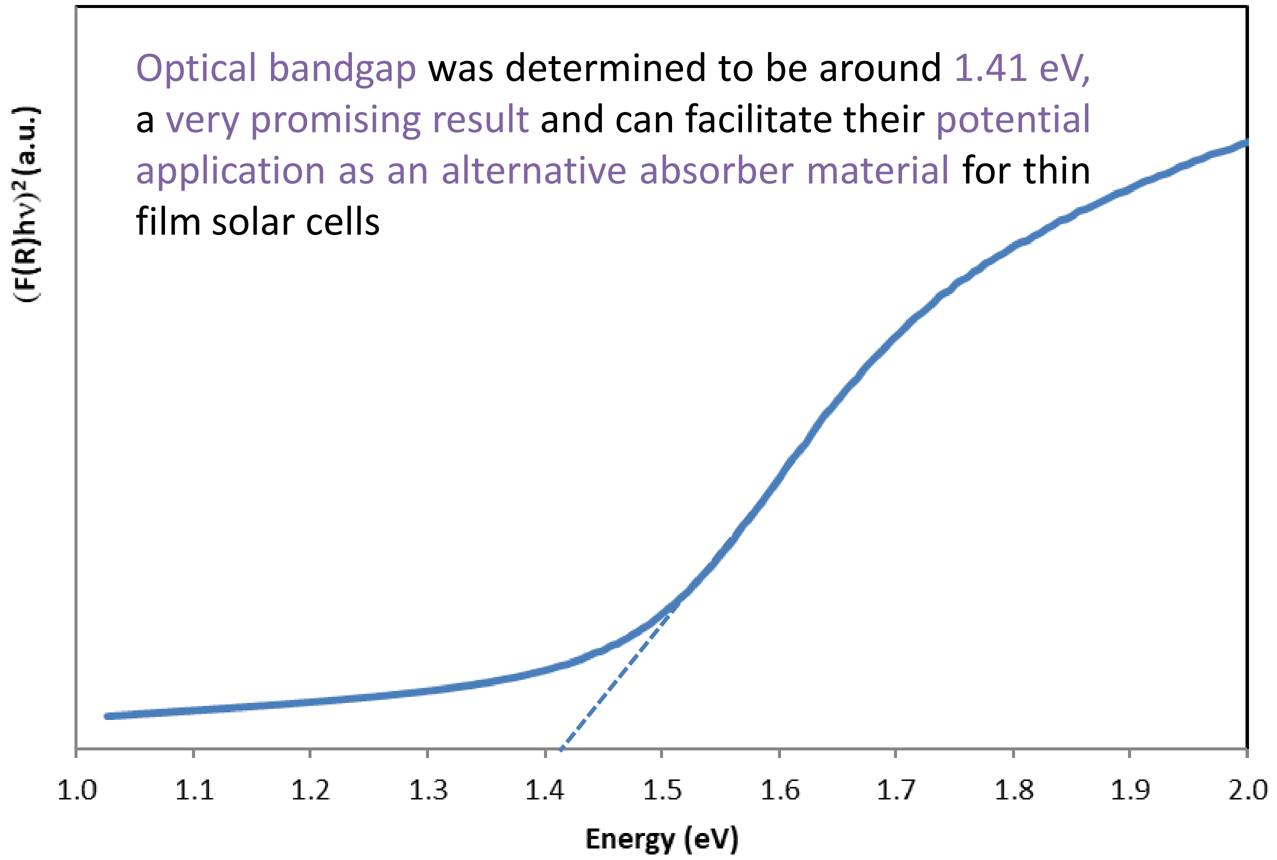
R_{exp}	R_{wp}
2.29	5.20

	HT	*MCS*	
Cryst. Size (nm)	141	*26*	
Lattice parameters			*standard values*
a (Å)	6.02	*6.02*	*6.018*
b (Å)	3.80	*3.80*	*3.7958*
c (Å)	14.50	*14.50*	*14.495*

The values obtained for the R factors (R_{exp} (expected R factor) and R_{wp} (weighted profile R factor) ensure the good level of the refinement

Results

Tauc plot for the 2 h MCS $CuSbS_2$ powders



The optical bandgap (Eg) estimation was performed by extrapolating the linear region of the Tauc plot to the horizontal axis and considering the intersecting point.

Final remarks

Powders of $CuSbS_2$ were synthesized directly through a short mechanochemical step

- orthorhombic structure with the space group Pnma (62)

Absence of any phase transformation with the heat treatment at 350 ^oC/24 h

- strong structural stability of the produced phase

The bandgap energy of the $CuSbS_2$ powders was estimated by extrapolation to be ~1.41 eV

- good agreement to the values reported in the literature

The mechanochemically synthesized $CuSbS_2$ compounds can be considered suitable to be used as absorber materials for thin-film solar cells

The MCS process is a viable and promising route for the preparation of materials for photovoltaic applications

Acknowledgements

LocalEnergy
Local Resources for Multifunctional Tetrahedrite-based Energy-Harvesting Applications

http://localenergy.lneg.pt

This work is funded by national funds through the FCT – Fundação para a Ciência e a Tecnologia, I.P., under the project PTDC/EAM-PEC/29905/2017

FCT Fundação para a Ciência e a Tecnologia

REPÚBLICA PORTUGUESA

Thank You

For Your Attention

filipe.neves@lneg.pt

HR EXCELLENCE IN RESEARCH