

LOCALENERGY - LOCAL RESOURCES FOR MULTIFUNCTIONAL TETRAHEDRITE-BASED ENERGY-HARVESTING APPLICATIONS

LOCALENERGY PROJECT CHARACTERISTICS

Website: <http://localenergy.lneg.pt/>

Consortium: Principal contractor - Laboratório Nacional de Energia e Geologia, I.P. (LNEG);

Participating Institutions: Associação do Instituto Superior Técnico para a Investigação e Desenvolvimento (IST-ID) and Associação para a Inovação e Desenvolvimento da Faculdade de Ciências e Tecnologia (NOVA.ID-FCT);

Research units: Centro de Ciências e Tecnologias Nucleares (C2TN), Centro de Investigação de Materiais/i3N (CENIMAT|i3N);

Consultant: Dr. Patrícia Carvalho, from SINTEF.

NOVELTY

Use of natural tetrahedrites, obtained from Iberian Pyrite Belt (IPB), for producing thermoelectric (TE) and photovoltaic (PV) materials.

EXCELLENT SCIENCE

Research performed in multiple scientific domains with multiple application levels comprising a multidisciplinary research team that involved researchers and institutions with proven record of achievements in the field of materials science, geology, and renewable energy.

INTEGRATION AND TRAINING OF YOUNG RESEARCHERS

The amount allocated to this item corresponded to the largest budget share (around 65%).

LONG-TERM VISION

- (a) Contribute to the development of sustainable energy harvesting systems based on low carbon energy technologies.
- (b) Contribute to a more circular economy by the recovery of raw materials from mining waste, transforming an environmental problem into an opportunity to recover valuable resources.
- (c) Exploitation of two Portuguese natural resources, namely, mineral resources and solar energy.

LOCALENERGY PROJECT OVERVIEW

LocalEnergy addressed research and development activities related with new TE and PV materials based on tetrahedrite. Tetrahedrite, one of the most abundant sulfosalt minerals in the earth's crust, is a class of copper antimony sulfosalt mineral with general formula $Cu_{12-x}(TM)_xSb_4S_{13}$ (TM = transition metal) and is considered a sustainable alternative for the current commercial TE and PV materials that contains rare and/or toxic elements. Therefore, two main objectives of the LocalEnergy project were: (1) evaluate the feasibility of the direct use of tetrahedrite-tennantite ore ($Cu_{12-x}(TM)_x(Sb,As)_4S_{13}$), collected in the IPB, in the processing cycle of materials for TE applications and (2) synthesis of materials based on tetrahedrite-tennantite and chalcocite (Cu_2S) for PV applications. In this context, the main achievements of this project can be summarized as follows:

GEOLOGICAL SETTING: TETRAHEDRITE-TENNANTITE MINERAL RESOURCES IN THE IBERIAN PYRITE BELT

Samples of tetrahedrite-tennantite ($Cu_{12-x}(TM)_x(Sb,As)_4S_{13}$) were collected from two distinct settings in the IPB. At Neves Corvo, the ore samples used in this study were collected underground from one of the intersected "dirty-copper" pockets of ore, while at the Barrigão Mine surface samples were collected from the widespread dumps.

The IPB is approximately 250 km long and 30-50 km wide from Alcácer do Sal in Portugal to Seville in Spain (**Fig. 1**) and is one of the

most outstanding ore provinces of Europe, hosting one of the largest concentrations of sulphides in the earth's crust. The Neves-Corvo polymetallic base metal mine is a world-class volcanogenic massive sulphide (VMS) deposit and the largest operating mine in Portugal. Seven massive sulphide bodies and related stockwork have been discovered to date, totalling 300 Mt of sulphides. The deposits are classified as VMS and typically occur as lenses of polymetallic (Cu, Zn, Sn, Pb) massive sulphides and stockworks that formed at or near the seafloor in submarine volcanic environments. The deposits are located near the top of a dominantly volcanic sequence of Late Devonian-Early Carboniferous age, 360-342Ma.

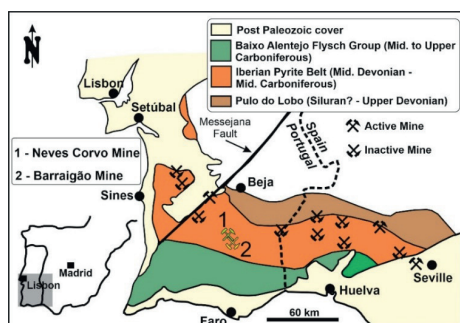


Fig. 1 – Simplified geological map of the Iberian Pyrite Belt with the location of the main mineral deposits.

Overlying the mineralisation there is a repetition of volcanic-sedimentary and flysch units, approximately 350 m thick. The whole assemblage has been folded into a gentle anticline orientated northwest-southeast, which plunges to the southeast, resulting in orebodies distributed on both limbs of the fold. All the deposits have been affected by both sub-vertical and low angle thrust faults, which has resulted in repetition and thickening of the massive sulphides, in some areas up to 30 m thick.

The Barrigão copper mine, also within the IPB, is in southern Portugal, about 10 km southeast from Neves Corvo (**Fig. 1**). Structurally, the mine consists of two converging metric thick vein structures, extending approximately 1800 m along strike. Several mine shafts were sunk down to a depth of 45m. The Barrigão copper ore is represented by fault breccias composed of chalcopyrite, minor tennantite, pyrite relics and arsenopyrite in a matrix of quartz and carbonates. Host rocks are Viséan shales and greywackes of the Baixo Alentejo Flysch Group. The age of the Barrigão mineralised structure and other similar copper structures present in the region (e.g., Brancanes, Ferrarias/Cova dos Mouros etc.) is considered late- Variscan and/or eo-Alpine. These structures are intimately related

with the main fault systems present in the SE sector of the South Portuguese Zone, striking generally NE-SW and NWSE. Exploitation of these veins took place mainly in the second part of the XIX century, sometimes down to a depth of 100 m.

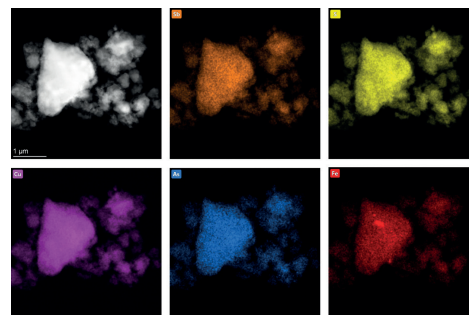


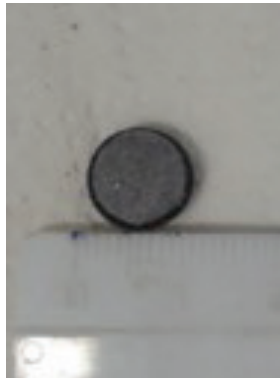
Fig. 2 – Typical transmission electron microscopy (HAADF-STEM) image and the corresponding elementary maps images for MCS particles of mixtures with 50% ore.

VALORISATION OF NATURAL RESOURCES: INCORPORATION OF NATURAL MINERAL TETRAHEDRITES FOR THERMOELECTRIC APPLICATIONS BY COMBINING MECHANOCHEMICAL SYNTHESIS AND HOT PRESSING

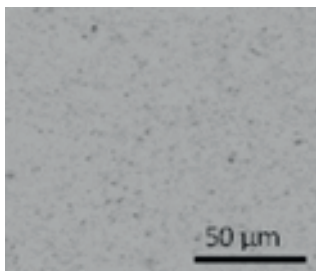
TE devices can directly convert heat into usable electricity, with tetrahedrite being considered a cheap and non-toxic TE material with good potential for applications. Mechanochemical synthesis (MCS) in a planetary mill was used to produce synthetic tetrahedrite powders from the elements Cu, Sb and S. Although the nominal composition, $Cu_{12}Sb_4S_{13}$ of tetrahedrite was used, minority phases identified as famatinite and skinnerite were detected with X-ray diffraction. The MCS of mixtures of synthetic and IPB ore tetrahedrite (in percentages from 10% to 80%), in a second milling, was carried out under conditions identical to those used for the initial milling. With the MCS process there was a complete dissolution of the synthetic tetrahedrite constituents with the main constituents of the ore, giving rise to the formation of a solid solution that can be generically expressed as $(Cu,Fe)_{12}(Sb,As)_4S_{13}$. Chemical mapping (**Fig. 2**) revealed that the main elements were evenly distributed across all analysed particles, with the exception of Fe, which has a stronger signal in some areas, probably associated with pyrite. Considering the initial constitution of the materials, the uniform distribution of Cu, Sb and As is extremely relevant. A single sulphide phase, identified as tetrahedrite-tennantite-(Fe), was obtained with the mixtures containing ore from the tailings of the Barrigão mine.



(a)



(b)



(c)

Fig. 3 – (a) Hot-pressing machine; (b) final pellet (10 mm diameter x 1 mm thickness); (c) Typical backscattered electron images: combination of 50% synthetic and natural mineral from the Barrigão mine.

Hot-pressing was used to produce pellets from the MCS powders (**Fig. 3**). The densification achieved was the desired for the intent application and without any phase decomposition (**Fig. 3**). For the TE properties, an in-house build system was employed for measuring the Seebeck (S) and electrical resistivity (ρ) from 30 to 300 K, which allowed the calculation of the power factor ($PF = S^2/\rho$) at room temperature. The obtained results demonstrated the feasibility of using tetrahedrite-tennantite ore from the IPB for processing tetrahedrite-based TE materials by combining MCS and hot-pressing.

OPTOELECTRONIC PROPERTIES OF AMORPHOUS COPPER-ARSENIC-SULPHIDE THIN-FILMS DEPOSITED VIA RF CO-SPUTTERING FOR PHOTOVOLTAICS

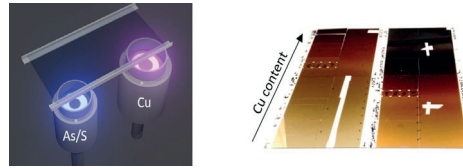


Fig. 4 – (a) Illustration of the radio-frequency co-sputtering setup, showing a 2-inch As/S target and a 3-inch commercial copper target and (b) two thin-films deposited on 20x10 cm glass substrates – the deposition conditions were identical, with the exception of the power applied to the copper target – 50 W (CS50) and 100 W (CS100).

Clean, decarbonized energy is crucial for the sustainability of the modern world. Therefore, it is needed a continuous, consistent effort in the employment of innovative technologies and materials that enable low or no carbon emissions. PV technologies represent a strong contender in reaching these goals, as they virtually have no carbon footprint stemming from energy generation. The possibility of depositing copper arsenic sulphide (CAS) compounds via radio frequency magnetron sputtering and of modifying their optoelectronic properties by tuning the stoichiometry makes them a promising candidate for application in thin-film PV technologies. In the scope of the LocalEnergy project, the 2-inch targets used for the sputtering deposition of As/S were obtained from the ore collected in the Barrigão mine and, subsequently, milled into a fine powder and pressed. In this work we studied the properties of co-sputtered amorphous CAS thin-films with thicknesses ranging from 90 nm to 300 nm, shown in **Fig. 5**. The sheet resistance reached a minimum value of $260 \Omega/\square$, with an element stoichiometry of 4.9:1:2.6 (Cu:As:S), revealing a Cu-rich phase. The films presented a wide bandgap of ~ 2.2 eV and 65% optical absorbance in the wavelength range of 300 to 600 nm. The results attained here represent the proof-of-concept for the deposition of CAS-based thin-film absorber materials with extremely tunable optoelectronic properties, evidencing the high potential for application in low-cost thin-film flexible solar cells.

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