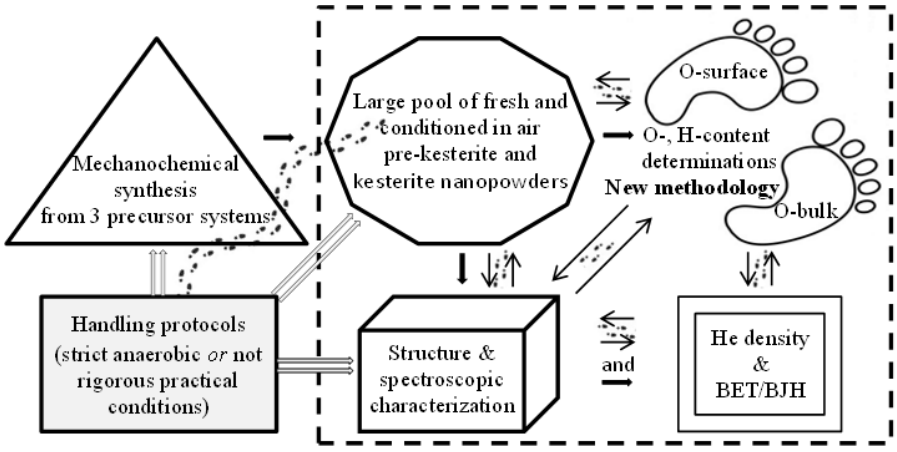
STUDY OF THE OXYGEN FOOTPRINT AND ITS SIGNIFICANCE IN THE KESTERITE Cu_2ZnSnS_4 SEMICONDUCTOR FOR NEXT GENERATION PHOTOVOLTAIC CELLS

Why oxygen-related study for non-oxide kesterite Cu_2ZnSnS_4? – The quaternary sulfide Cu_2ZnSnS_4 (kesterite) is a front runner direct semiconductor material for the next generation of affordable and environment-friendly photovoltaic (PV) cells to replace for sound reasons the currently utilized Si (various forms of silicon), CdTe (cadmium telluride), and CIGS (copper indium gallium diselenide). Kesterite is a non-oxide semiconductor and its electronic properties will depend on non-intentional O-substitutions in the preparation stage whereas its long-term stability and functionality in device applications will rely on the material's susceptibility to oxidation in humid air. This can be acutely true for the nanopowders with high specific surface area and increased propensity for chemisorption of oxygen and water vapor. Prolonged exposure to air could likely be then associated with progressing moisture-assisted oxidation. The crucial O-aspects are mostly unrecognized in studies on kesterite with scarce non-systematic reports on the subject.

This proposal is intended to constitute the first comprehensive study focused on the O-related repercussions in kesterite preparation and storage in ambient air. For this, various kesterite nanopowders will be made by the convenient mechanochemically assisted synthesis route mastered in the PI's group. In stage 1, high energy ball milling affords cubic pre-kesterite with no semiconductor properties, which in stage 2 upon annealing at 500-600 °C yields the tetragonal kesterite semiconductor, E_g = 1.4-1.5 eV.

Unique direct determinations of oxygen and hydrogen contents – Until recently no direct determination of oxygen in inorganic materials has been possible due to analytical constraints. The total O-content could only be estimated by difference from 100 % of other elements known contents. With the recent advent in analytical instrumentation it is now possible to do such determinations for kesterite and other inorganic materials. This proposal is the first attempt to utilize the state of the art oxygen-nitrogen-hydrogen analyzer (Leco ONH836, originally designed for O-, N- and H-analyses in metals) for direct oxygen and hydrogen determinations in kesterite nanopowders using a recently elaborated by us dedicated methodology. Several supplemental methods are to be used to interpret the elemental analysis data and provide with the materials extensive structural and spectroscopic characterization.

Flow chart of key project stages



Oxygen footprint? – Directly determined O- and H-contents, both total and in specific groups *via* original methodology, will be traced for 3 mechanochemical preparation routes, each using different substrates, *via* pre-kesterite to freshly made and, later, conditioned in air kesterite nanopowders. Also, 2 distinct sample handling protocols will be applied. The evaluated O-trace for each route will define crucial steps in O-acquisition and the time effect on exposure to air. The wide range of the substrates, by-products, and final nanopowders will constitute an abundant pool of materials for detailed studies and cross-check data analysis. At the core of proposal – the various O-contents will be related in the context of overall composition to structural data, contaminations, He density/specific surface area, thermal stability, and spectroscopic properties including the essential energy bandgap characteristics.

The results will also clarify mechanistic aspects of the synthesis routes and quantify the structural/bulk *vs.* surface/volatile O-contents. They will be helpful in the synthesis optimization.

It is hoped that the project is well-focused and will offer an exemplary approach for others to address the rarely explored O-aspect in non-oxide materials. It should also be relevant to many studies on oxidation susceptibility and intentional O-doping of a variety of materials in electronics and ceramics.