Synthesis and crystal chemistry of materials for energy conversion: copper sulfides and oxy-sulfides for thermoelectricity

PhD thesis from the University of Rennes 1 (2021-2024) under the supervision of Pierric Lemoine (CR CNRS) and Carmelo Prestipino (CR CNRS)

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The generation of electricity from waste heat through thermoelectric conversion is emerging as a promising alternative energy source for the future. In this context, the design of new low-cost and high-performing thermoelectric materials constitutes a major technological. In recent years, copper-based sulfides with complex structures have been considered as promising thermoelectric candidates to replace materials derived from the binary Bi_2Te_3 presenting cost, safety, and environmental issues.[1] However, before the widespread use of copper sulfides for thermoelectric applications, such materials must udergone to an optimization procedure acting on composition, structure, and microstructure that requires a fine understanding of structure-properties relationships.[2] On the other hand this requirement is particularly changeling due to complex crystallographic structure and/or microstructure that are often prerequisites for performant thermoelectric materials. As a consequence, these structural studies require the combination of complementary characterization techniques and not conventional approaches.

For future applications, chemical stability, especially at high temperatures, is also an important parameter. From this point of view, copper sulfides show extensive room for improvement, with the maximum operating temperature around 700 K - 800 K, limited by materials decomposition.[3] This temperature limit could be increased by the incorporation of oxygen into the structure, then leading to the formation of oxy-sulfides. In fact, the strong hybridization of the oxygen and sulfur valence orbitals promotes higher chemical stability with respect to sulfide. Besides, this anionic mix would make it possible to modulate the electrical properties of materials, by making it possible to control the width of the "band-gap", and therefore opening up perspectives towards photovoltaics or water-splitting application.[4]

Oxy-sulfides are currently very little studied for their thermoelectric properties with the exception of those containing bismuth such as BiCuOS, Bi_2OS_2, Bi_2O_2S or $LaOPbBiS_3$.[5] Therefore, the study of these materials could present several prospectives: (i) improve temperature stability i.e. increase the operating temperature limit for applications, (ii) modulate the electrical properties by adjusting the level of order and substitution between oxygen and sulfur, (iii) develop a new family of bismuth-free thermoelectric materials.

This PhD thesis focuses on materials chemistry for energy conversion, a strong theme of the CSM-ISCR team.[6] During this PhD thesis will be carried out (i) the study of crystallographic structures and the structure-property relationships of thermoelectric copper sulfides with complex structures and (ii) the partial substitution of sulfur by oxygen aiming to develop a new family of bismuth-free thermoelectric materials with better temperature stability. Syntheses of the oxy-sulfides samples will be carried out in sealed tube from elemental or binary precursors, or by hydrosulfurization/oxydation, using the devices present in the laboratory. Structural studies will be carried out by using complementary characterization techniques (including large instruments): X-ray, neutron and electron diffraction on powder and single crystal and spectroscopic technics. Thermal stability will be studied *in situ* both in the laboratory by calorimetry and diffraction and on large instruments. Thermoelectric properties will be studied as part of the collaboration that exists since 2014 between the CSM team and the CRISMAT laboratory in Caen (France).

Candidate Profile

The candidate should have a master degree in materials science/chemistry. He/she should be motivated by fundamental research, well organized, meticulous and interested in solid-state chemistry and structural characterization techniques. Particular attention will be paid to applications from students with experiences on large-scale facilities and/or thermoelectric materials. Experience on coding (Python, C, Fortran) will be appreciated.

Practical aspects

This PhD thesis in materials science will starts in October 2021 at the Chemical Science Institute of the University of Rennes 1. The candidates have to send their cover letter, CV, copy of the highest diploma with transcript recording of their grades, recommendation letters … at https://theses.doctorat-bretagneloire.fr/3m.

Candidates opened until 28/05/2021

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