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

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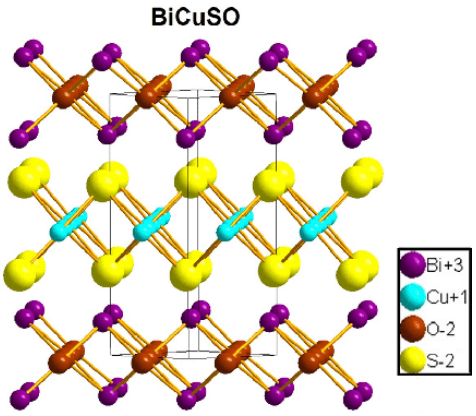
The generation of electricity from waste heat through thermoelectric conversion is emerging as a promising alternative energy source for the future. In this context, the design of new thermoelectric materials of high performance at low cost and non-toxic constitutes a major technological challenge.

In recent years, copper based sulfides with a complex structure have been considered one of the most promising thermoelectric materials to replace the best current materials derived from the binary Bi_2Te_3[1]. Indeed, copper sulfides can be prepared in large quantities, are generally formed of elements non-toxic, non-strategic, and inexpensive.



Crystal structure of BiCuSO[5]

The optimization of these materials for application by chemical substitutions or alternative synthetic route requires an understanding of the relationships between the structure to properties. However, due to their complex crystallographic structures and microstructures, these studies require the combination of complementary characterization techniques such as X-ray, neutron, and electron diffraction.

The study of the chemical temperature stability is also an important parameter to be taken into account for future applications. From this point of view, copper sulfides are materials for which the temperature operating range is limited to 700 K - 800 K, above that the materials start to decompose.[2,3] This temperature limit could be increased by incorporation of oxygen into the materials, then leading to the formation of oxy-sulfides. In fact, the strong hybridization of the oxygen and sulfur valence orbitals improves the chemical stability of these materials. In addition, 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.[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, it seems interesting to study the properties of these materials for several reasons: (i) increase the limit temperature of use to improve temperature stability, (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 Master 2 internship focuses on materials chemistry for energy application, a strong theme of the CSM-ISCR team, it should continue with a doctorate starting in October next year. During this internship will be carried out (i) the study of crystallographic structures and the structure-property relationships of thermoelectric copper sulfides with a complex structure (germanites $Cu_{22}Fe_8Ge_2Sn_2S_{32}$ and $Cu_{22}Fe_8Sn_4S_{32}$, renierite $Cu_{20}Zn_2Fe_8Ge_4S_{32}$ and stannoidite $Cu_8Fe_3Sn_2S_{12}$) and (ii) the partial substitution of sulfur by oxygen with the aim of developing a new family of bismuth-free thermoelectric materials with better temperature stability.

The syntheses of the oxy-sulfides samples will be carried out in a sealed tube or by hydrosulfurization/controlled oxidation, 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. 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 has existed since 2014 between the CSM team and the CRISMAT laboratory in Caen.

Candidate Profile

Attending master in material science / chemistry.

The candidate should be motivated and interested in solid-state chemistry and structural characterization techniques. Particular attention will be paid to applications from students wishing to pursue with a doctorate. Experience on coding (Python, C, Fortran) will be appreciated.

Practical aspects

The duration of the stage is of 5 months, to be completed in the period between the 15 of January and the 20 of July depending from the student University requirements. The net salary for month is 591.51€, and the cost of a room in the university residence span between 164€ to 350€.

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References

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