Theoretical Study of Thermoelectric Antimonides for Very High Temperature Applications

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The PhD project is part of the HIGHTHERM project that focused on materials with potential industrial applications at temperatures above 600°C to harvest waste heat and convert it into usable energy, for instance the glass industries. To meet such requirements, HIGHTEM project deals with the research and development of high temperature thermoelectric materials based on the cubic structure Th_3P_4. Within this family, *n*-type La_3Te_{4-x} are good thermoelectrics with ZT above the one at 1000°C. However, there is little information about their p-type counterparts (anti-Th_3P_4 antimonides) with however proof of their good performance (ZT slightly below the unity at high temperature); the study, the optimization and the implementation within thermoelectric unilegs (coupled to *n*-La_3Te_{4-x}) of these p-type materials are the focus of this proposal. HIGHTEM aims at proposing to ultimately make a demonstrator using these *n* and *p* type materials that will be test in real life condition at St Gobain CREE. The consortium combines the expertise of well know research centers: CRISMAT laboratory, ISC Rennes, NIMS Tsukuba via the UMI LINK, and an end user: St Gobain via the CREE research center and also via its belonging to the LINK UMI.

With the development of powerful methods to compute the electronic band structure of solids and the increasing complexity of the formulations of advanced thermoelectric materials such as those targeted in this project, quantum chemical calculations based on density functional theory (DFT) are necessary tools for the optimization of thermoelectric material properties. DFT programs embedding the most advanced approximation of the exchange-correlation functionals and considering relativistic effects will be employed to calculate the electronic structures required to use a band engineering approach for the optimization of the thermoelectric properties of the studied materials. More specifically, collected data from experiments (LINK, CRISMAT) will be used to provide significant insights to explain and understand the electrical properties of the new synthesized materials, as well as to predict how the selected structures/compositions can form ideal candidates for thermoelectricity.

To gain further information in the electronic transport properties, Boltzmann transport theory will be combined with band structure calculations assuming a constant relaxation time. Vibrational properties (low-energy phonon band structures, Grüneisen parameters) will also be studied using the density functional perturbation theory in order to gain some information on the thermal conductivity. The theoretical results, which will be gleaned, should demonstrate a complete feedback loop with theory guiding material synthesis and experiments for testing predictions, and theory refined by the experimental results.

The PhD project will start in Fall 2020 in Rennes in the Inorganic Theoretical Chemistry (CTI) team, in the Institute of Chemical Sciences of Rennes. The CTI team gathers several theoreticians with complementary skills in theoretical chemistry but also physics, working with a broad set of quantum chemical tools, ranging from high precision *ab initio* wavefunction-based calculations to fast semi-empirical methods. A stay at NIMS, Tsukuba (Japan) is envisioned (for few months). Applications are already open and candidates shall contact R. Gautier (rgautier@ensc-rennes.fr) with a CV and a motivation letter.

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