Master Thesis Topic
(February – July, 2025)

Title of the research topic	Derivatives of Na-thioantimonate as solid electrolytes for all-solid-state batteries
Laboratories	**Laboratoire de Réactivité et Chimie des Solides (LRCS)** **Laboratoire de Physico-Chimie de l'Atmosphère (LPCA)**
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Scientific Project:

Today, the most competitive and reliable technology used in electrochemical storage systems is based on lithium (Li) and the use of ionic conductive liquids. Considering the rising cost of lithium raw materials, the risks associated with their supply (abundance, geographical localization…) and the use of flammable liquids, it is necessary to find and offer alternatives involving other metal components and greater safety. Sodium (Na)-ion all-solid-state batteries (Na-ASSBs) are seen as an interesting option, combining a more abundant, and cheaper element with the use of a solid ionic conductor (non-flammable)[1].

Sulphur-based compounds are promising solid electrolytes. They are ductile, enabling good cold-pressed electrolyte/electrode contacts, and highly conductive. Among them, compounds based on the Na_3PnCh_4 formula, with Pn and Ch as pnictogen and chalcogen elements, attract attention[2]. With phosphorus (P, element Pn) and sulphur (S, element Ch), sodium tetrathiophosphate Na_3PS_4 is probably the most studied Na-solid electrolyte (ionic conductivity around 10^{-4} S/cm). A great deal of research has gone into improving it, including doping and iso/alio-valent substitutions on both the Pn and Ch sites[3]. A remarkable development in this field has been the design of sodium thioantimonate Na_3SbS_4 with a conductivity of 1.1 x 10^{-3} S/cm, a low activation energy of 0.20 eV and good moisture stability[4], unlike Na_3PS_4. To date, few studies have been carried out on Na_3SbS_4 derivatives.

The current project aims to explore $NaSbS_2$ and Na_3SbS_4 phases by attempting to replace antimony (Sb) with bismuth (Bi, pnictogen element) in order to prepare $NaSb_{1-x}Bi_xS_2$ or $Na_3Sb_{1-x}Bi_xS_4$-type phases. Bismuth has never yet been proposed as substitute. The targeted materials will be synthesized by mechanochemistry and characterized in detail by various structural, microstructural and electrochemical techniques.

Techniques used:

Ball-milling synthesis, Thermal analyses, Raman spectroscopy, Scanning electron microscopy, Impedance spectroscopy, X-Ray diffraction, Electrochemical cycling.

Recent publications related to the topic:

1. R. Usiskin et al., Nature Rev. Mater. 6 (2021) 1020.
2. S. Ohno et al., Progess Energ. 2 (2020) 022001.
3. T. Fuchs et al., ACS Energy Lett. 5 (2020) 146−151 / N. Tanibata et al., RSC Adv., 4 (2014) 17120–17123 / X. Feng et al., Adv. Functional Mater. 29 (2019).
4. A. Banerjee et al., Angew. Chem. Int. Ed. 55 (2016) 9634 –9638.

Documents to provide: We wish to hire a highly motivated Master student with skills in inorganic chemistry and interest in synthesis. Please provide Curriculum vitae and motivation letter.