



## Master Thesis Topic (February – July, 2025)

<b>Title of the research topic</b>	<b>NaSb<sub>1-x</sub>Bi<sub>x</sub>S<sub>4</sub> as solid electrolyte for all-solid-state batteries</b>
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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)<sup>1</sup>.

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<sub>3</sub>PnCh<sub>4</sub> formula, with Pn and Ch as pnictogen and chalcogen elements, attract attention<sup>2</sup>. With phosphorus (P, element Pn) and sulphur (S, element Ch), sodium tetrathiosphosphate Na<sub>3</sub>PS<sub>4</sub> is probably the most studied Na-solid electrolyte (ionic conductivity around 10<sup>-4</sup> 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<sup>3</sup>. A remarkable development in this field has been the design of sodium thioantimonate Na<sub>3</sub>SbS<sub>4</sub> with a conductivity of 1.1 x 10<sup>-3</sup> S/cm, a low activation energy of 0.20 eV and good moisture stability<sup>4</sup>, unlike Na<sub>3</sub>PS<sub>4</sub>. To date, few studies have been carried out on Na<sub>3</sub>SbS<sub>4</sub> derivatives. The current project aims to explore Na<sub>3</sub>SbS<sub>4</sub> phase by attempting to replace antimony (Sb) with bismuth (Bi, pnictogen element) in order to prepare Na<sub>3</sub>Sb<sub>1-x</sub>Bi<sub>x</sub>S<sub>4</sub>-type phases. Bismuth has never yet been proposed as substitute. The targeted materials will be synthesized by high-temperature reactions or by mechanochemistry and characterized in detail by various structural, microstructural and electrochemical techniques.

### **Techniques used:**

High-temperature reactions and 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., Progress Energy. 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.