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PhD Position in Solid-State Chemistry 2024

Design of Novel Soft Chemical Syntheses for Controlling Anionic Redox Topochemistry of Chalcogenide Materials

Context:

Precise manipulation of atomic arrangements is a fundamental approach for tailoring materials with specific functionalities. In our bodies, numerous enzymes cut or connect specifically targeted chemical bonds, building up complex molecular structures. These intricate natural processes are now within reach of mankind thanks to, e.g. modern genome-editing technologies and organometallic coupling reactions, offering vast prospects in materials design.

Our team envisions a similar horizon with those molecular chemistry, but rather aims at non-molecular inorganic solids like metals, ceramics, and minerals. Stepwise and controlled structural transformations are well known also in solid-state chemistry with the term 'Topochemistry', but its versatility as a tool of chemical bond editing was limited compared to those in molecular systems. We recently proposed a novel type of topochemistry that can cut fully covalent, anionic chalcogen-chalcogen (Ch-Ch) bonds through redox reaction with external species (Fig. 1, also see ref [1]). This anionic redox topochemistry opens a space between the redox-inert 2D slabs by unfastening covalent Ch-Ch bonds, leading to either insertion of guest atoms [2] or deintercalation of those disrupted Ch atoms from the material [3]. These manipulations of covalent bonds, mimicking the process that open and close a zipper, pave the way for exploring unprecedented layered materials, with possible electronic, magnetic, optical, and catalytic functionalities.

Over the recent few years, we have carried out a series of the proof-of-concept experiments demonstrating those novel synthetic routes and succeeded in preparing a handful of novel metastable phases [1]. From this year, we are running French National Agency for Research (ANR) – funded project 'COBEDIT' aiming at evolving this anionic redox topochemistry into a versatile toolbox for editing covalent bonds in inorganic chalcogenide materials.

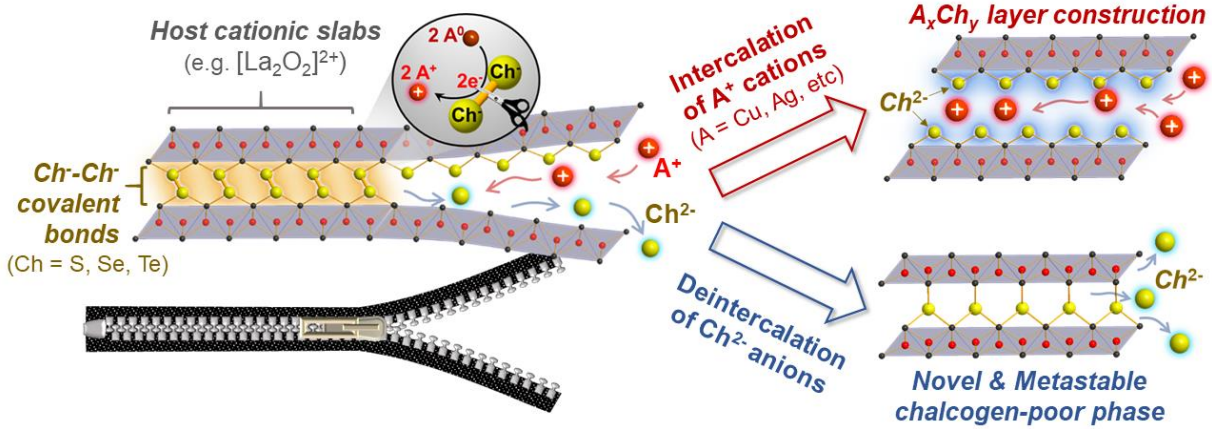

Fig. 1. Schematic illustration of 'zipper-type' topochemistry driven by redox activity of anionic chalcogen dimers $[Ch_2]^{2-}$ (Ch = S, Se, Te) that joins up the redox-inert 2D slabs.

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PhD project:

This PhD thesis constitutes the main part of the ANR-funded project 'Covalent-bond editing by topochemistry of chalcogenide materials (COBEDIT)' that pursues exploratory syntheses employing this novel anionic redox topochemistry. The candidate will work on: 1) design of reagents, precursors and reaction conditions (ceramic, solvothermal, Schlenk techniques, electrochemistry etc.) to steer the anionic redox topochemistry toward targeted directions, 2) characterization of products by X-ray and electron diffractometry, electron microscopy, Raman spectroscopy, magnetometry and other bulk or local probes, as well as 3) experimental & computational investigation of reaction dynamics behind selectivity between competing reactions. At the end of the project, this multi-faceted approach will allow design of unprecedented chalcogenide materials through cutting or forming covalent anion-anion bonds in a stepwise and controlled manner.

Candidate profile:

Candidates must hold a master's degree or an equivalent one (e.g. a diploma of an engineering school) with a firm record of training in solid-state chemistry or materials science. Experiences in syntheses of solid-state materials, crystal chemistry and materials physics will be an asset. The project involves close collaborations with experts in syntheses, computational chemistry, crystallography, and condensed matter physics. The successful candidate is accordingly expected to have good ability for team work and dynamism on learning new skills. Applicants must be fluent in English and/or French with competences in scientific writing.

Scientific environment:

The project will take place at the Institut des Matériaux de Nantes Jean Rouxel (IMN; https://www.cnrs-imn.fr/), one of the main materials research centers in France, bringing together more than 110 permanent staffs and 90 research contractors. The selected candidate will be hired in the "Physics of Materials and Nanostructures" team and will work in the framework of the chalcogenide transverse axis of the laboratory. This PhD project is funded by ANR with remuneration around 2135 € gross/month from 01/10/2024 onwards.

How to Apply:

All application must be made, with a CV and a cover letter as supporting documents, through our HR portal site:
https://emploi.cnrs.fr/Offres/Doctorant/UMR6502-SHUSAS-001/Default.aspx?lang=EN

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Related publications:

[1] Sasaki et al. Anionic Redox Topochemistry for Materials Design: Chalcogenides and Beyond. *ACS Org. Inorg. Au* **2023**, DOI: 10.1021/acsorginorgau.3c00043.
[2] Sasaki et al. Topochemical Approach to Synthesize Layered Materials Based on the Redox Reactivity of Anionic Chalcogen Dimers. *Angew. Chem. Int. Ed.* **2018**, *57*, 13618.
[3] Sasaki et al. Design of Metastable Oxychalcogenide Phases by Topochemical (de)Intercalation of Sulfur in $La_2O_2S_2$. *Nat. Commun.* **2021**, *12*, 3605.