PhD Opportunity: New Functional Oxides by Crystallisation of Amorphous Precursors

The project:

This is an exploratory solid-state chemistry project which aims to discover new oxide materials using unconventional non-equilibrium synthesis methods. The project will make use of laser-assisted aerodynamic levitation melting in parallel with mechanical activation techniques as a route to metastable compounds with new compositions and crystal structures, with potential functional properties including ionic conductivity, optical transparency, luminescence or ferroic properties. The synthesis work will be partially supported by composition-prediction calculations in collaboration with the University of Liverpool (U.K.). The prepared materials will be characterized at multiple length scales and temperatures: this will include powder diffraction methods (e.g. non-ambient PXRD <2000°C using the in-house high-temperature platform; and ab-initio structure solution from synchrotron X-ray diffraction and neutron diffraction data), high-resolution transmission electron microscopy using state-of-the-art instrumentation (available for diffraction, STEM-HAADF, EELS and high-temperature in-situ measurements), and high-temperature high-field solid-state NMR. Property measurements (e.g. impedance spectroscopy) will be conducted both in-house and with established external collaborators including international partners.

The context:

At CEMHTI (CNRS UPR3079), we are pioneering the use of containerless aerodynamic levitation (ADL) apparatus with laser heating to synthesise precursor glasses and melts of diverse compositions, and crystallising these at relatively low temperatures to produce highly dense oxide ceramics with new compositions, crystal structures and/or microstructures that host desirable physical properties for optical and ionic transport applications (http://www.cemhti.cnrs-orleans.fr/instruments/levitation.aspx). Using this method, we have recently isolated new melilite-type oxide ion conductors (doi.org/10.1021/acs.chemmater.0c03441) and new luminescent YAG materials with extraordinary non-stoichiometric compositions (European patent application N° 21305159.2; manuscript in preparation). In parallel with ADL, this project will expand the glass/melt-crystallisation synthesis concept by using mechanical activation methods (e.g. high energy ball milling) to produce amorphous precursors at low temperatures, allowing access to a wider range of compositions. This PhD position is funded by the ANR project “CAPRE”.

The candidate:

We would welcome applicants with a good undergraduate degree in the physical sciences (e.g. chemistry, materials science, physics) who have completed a masters project related to solid state science. The successful candidate will join a team of PhD students and engineers with a range of international backgrounds, and may have opportunities to travel to access specific expertise and facilities. The University of Orléans offers teaching experience. Funding for 3 years is available. A starting date of October – November 2021 is envisaged.

Selected recent publications from the team:

“*Highly non stoichiometric garnet ceramics for optical function”*, European Patent Application N° 21305159.2 (2021)

“*$La_2Ga_3O_{7.5}$: A metastable ternary melilite with a super-excess of interstitial oxide ions synthesized by direct crystallization of the melt”,* Chemistry of Materials (2020) doi.org/10.1021/acs.chemmater.0c03441

“*Cooperative mechanisms of oxygen vacancy stabilization and migration in the isolated tetrahedral anion Scheelite structure”*, Nature Communications (2018) doi.org/10.1038/s41467-018-06911-w

“*Pressureless glass crystallization of transparent yttrium aluminum garnet-based nanoceramics”*, Nature Communications (2018) doi.org/10.1038/s41467-018-03467-7

“*Accelerated Discovery of Two Crystal Structure Types in a Complex Inorganic Phase Field”*, Nature (2017) doi.org/10.1038/nature22374

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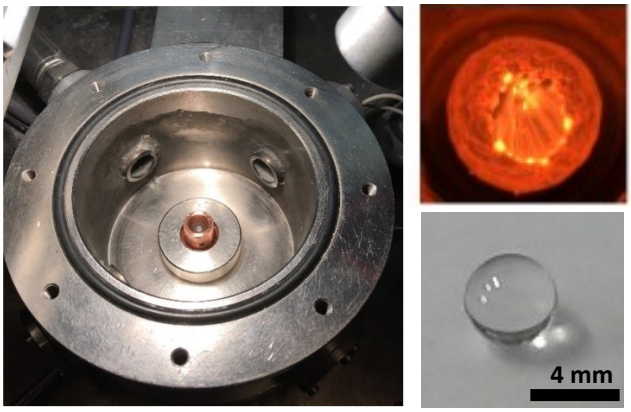
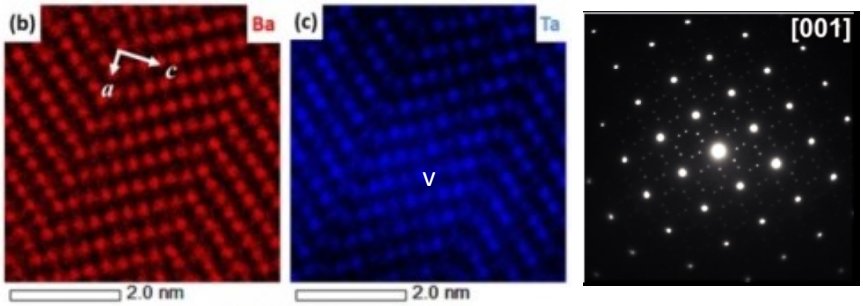
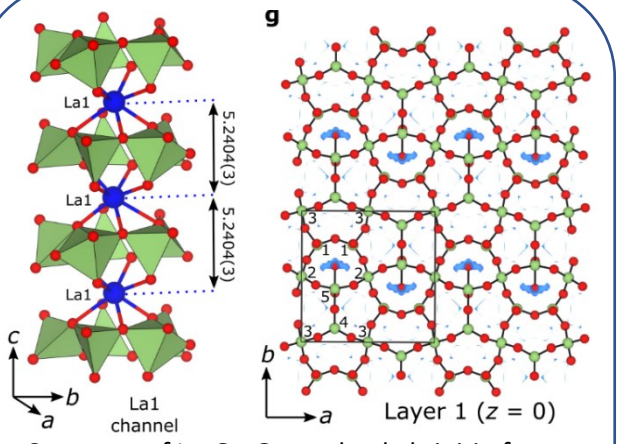


Aerodynamic levitation nozzle for laser-melting

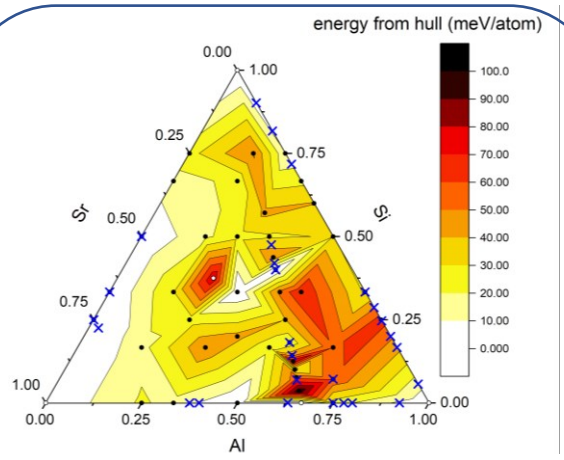
High-field NMR @ CEMHTI



In-house TEM data. (Left, centre) Atomic-resolution STEM-EDX images; (right) selected-area electron diffraction pattern



Structure of $La_2Ga_3O_{7.5}$, solved ab-initio from neutron + synchrotron powder diffraction data



Energy contour map of SrO-Al_2O_3-SiO_2 compositions calculated by the probe structure method