

**Internship proposal 2011-2012**

**Laboratory :** Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC)

**Address :** 4, Place Jussieu, 75252 Paris Cedex 05

**Laboratory director :** Bernard Capelle

**Internship supervisor :** Guillaume Ferlat (IMPMC)

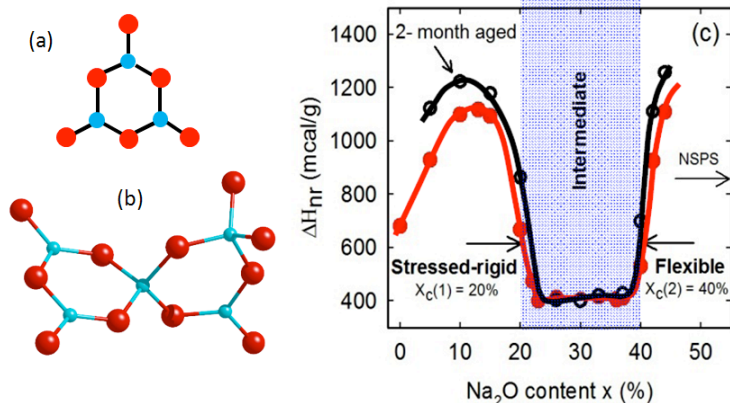
**Phone :** 01 44 27 98 22

**e-mail:** ferlat@impmc.upmc.fr



**Rigidity and structural transitions in borate glasses**

**Scientific project:** Borates (such as  $(M_2O)_x-(B_2O_3)_{1-x}$  where M is an alkali metal) enter in the composition of many technologically-important materials: electrolytes, waste glasses, bioactive materials, etc. From a microscopic point of view, the originality of borates, as compared to other glasses such as silicates, lies in the fact that boron can adopt several coordination states ( $^{3}B$  or  $^{4}B$  at ambient pressure) depending on the temperature and/or alkali concentration: this gives rise to original topological networks, which are made by both 2D (**figure (a)**) and 3D (**figure (b)**) superstructural units. These structural aspects are essentials to understand the many anomalies (density maxima,  $T_g$  minima) and several spectacular variations (**figure (c)**) of the properties with the alkali concentration  $x$ .



Examples of super-structural units (a) 2D boroxol ring (b) metaborate unit (c) Variation of the enthalpy associated to the glass transition as a function of the concentration  $x$  in  $(Na_2O)_x-(B_2O_3)_{1-x}$  systems: three distinct phases are observed: rigid, intermediate and flexible.

This project is motivated by the recent discovery (**figure (c)**) in  $(Na_2O)_x-(B_2O_3)_{1-x}$  glasses, of a so-called *intermediate phase*, in a given concentration range ( $20 \leq x \leq 40 \%$ ). This phase is, mechanically speaking, intermediate between the rigid and flexible phases. It is characterised by many remarkable properties: low enthalpy of vitrification (quasi-reversible glass transition), almost no aging over time, stress-free nature of the network, negative thermal expansion, etc. Interestingly, such an intermediate phase can also be obtained under high pressure. This highlights strong analogies between concentration- and pressure-effects: indeed both affect the network connectivity.

The aim of this project is to carry out **ab-initio molecular dynamics** of **borate glasses** for concentrations corresponding to the 3 phases (rigid, intermediate, flexible). These simulations will allow to i) determine the relevant super-structural units at each concentration ii) to calculate their experimental signatures (Raman, NMR, IXS) iii) to correlate these units to the rigidity properties (collaboration with M. Micoulaut, LPTMC). We shall then explore the effects of pressure and temperature for selected compositions, the aim being to be able to predict a pressure-temperature-composition phase diagram of rigidity. This project will be carried out in close connection with experimentalists (L. Cormier, G. Lelong at IMPMC and P. Boolchand, USA).

[1] G. Ferlat et al., Phys. Rev. Lett. **101**, 065504 (2008).

**Techniques in use:** (ab-initio) molecular dynamics simulations

**Applicant skills:** Solid background in solid-state physics and/or statistical mechanics. A basic knowledge of the molecular modelling techniques and/or the quantum-chemistry calculations is a plus. Skills in programming are appreciated but not mandatory.

**Granted internship :** yes ( 400 €/month)

**C'nano IdF laboratory (France only):** yes

**Possibility for a thesis :** yes (type of grant: French minister)