Synthesis, characterizations and shaping of cluster materials for the design of solar glass control.

Keywords: transition metal clusters, solid stae chemistry, crystal structures, electronic structures, optical properties, integration, composite films, surface coatings

Context. The PhD work will be made in the frame of the ANR project CLIMATE involving an international collaboration between the team Solid State Chemistry and Materials from the 'Institut des Sciences Chimiques de Rennes', the laboratory UMI LINK 3629 in Tsukuba (Japon) and Saint-Gobain Recherche (Aubervilliers).

Goals. CLIMATE aims at designing new materials for saving energy applications using a strategy that combines theory and experiments. Building with solar control glass must (i) reduce the heat gain inside the building, and thus reduces electricity and cooling costs and (ii) allow optimum light (natural daylighting) inside the building, and thus reduces the cost for artificial lighting during the day. CLIMATE aims to (i) develop composite materials based on metal clusters with UV absorption and infrared selectivity properties to incorporate them in a silica matrix and (ii) study their use as a nanocomposite coating for the design of glazing solar control.[1, 2]

The proposed PhD work will initially consist of developing, optimizing the composition and characterizing clusters functional building blocks with both good absorption in the UV and in the near IR. In a second step, these building blocks will be used for the functionalization of glass surfaces by thin-film deposition processes of functional hybrid silica. These functional building blocks of formula $[M_6X^i_{12}X^a_6]^{n-}$ (M = transition element, X = halogen) consist of an M_6 octahedral cluster surrounded by 12 inners ligands bridging the edges of the octahedron and by 6 terminal ligands (Fig. 1). The work will focus on the synthesis of new compounds based on $[\{Ta_{6-x}M'_xX^i_{12}\}X^a_6]^{n-}$ heterometallic clusters (M'= Nb, Mo or 3d element) and then to the study of their optical properties in the solid state, in solution and after deposition. The experimental work will be optimized by a computational approach consisting in studying the electronic structures of the targeted units and their optical and vibrational properties.

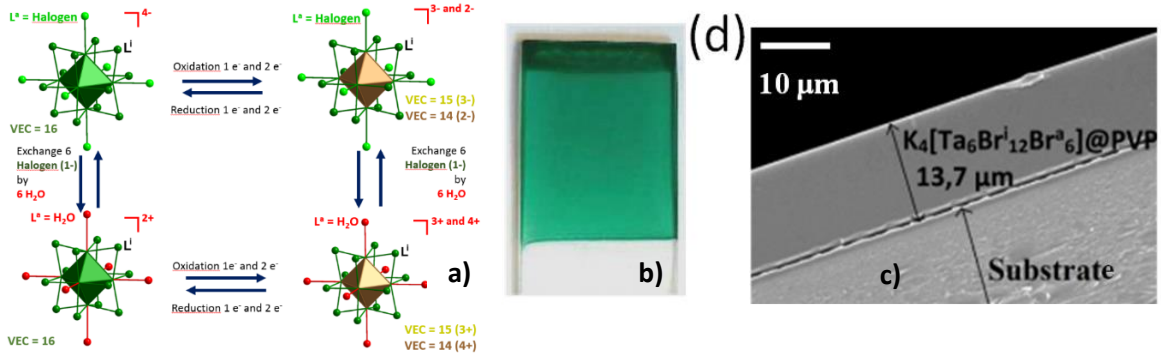

Figure 1. a) Representation of the evolution of the electronic counts, the charges and the properties of $[M_6X^i_{12}X^a_6]^{n-}$ according to the mechanisms of oxydo-reduction and ligand exchange. Images (b) of a cluster composite deposited on a glass slide and (c) scanning electron microscopy of the same sample.

The thesis work will consist of: (i) synthesizing inorganic compounds by high temperature solid state chemistry, (ii) computing the electronic structures and simulating the vibrational and optical properties of the new cluster units, (iii) optimizing syntheses of new phases (use of a specific DSC), (iv) measure the optical and vibrational properties in the solid state, in solution and in silica-based matrices, (v) prepare coating solutions and make surface modifications of the glasses (vi) determine the physico-structural, optical and mechanical properties of the compounds and of the functional surfaces obtained. The recruited candidate will be required to spend six months at Tsukuba's UMI LINK as well as several short stays at the Saint-Gobain Center in Aubervilliers.

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