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Prospection for original Inorganic oxides; attracting Structural, Electronic/ionic and Magnetic Properties towards Functional Materials.

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Context: The search for new functional materials constitutes an important challenge in the context of societal needs for renewable energy, optic, data-storage, nano-electronics … etc, see early recommendations from 2002 (1). In that purpose, academic research toward innovative materials is essential for the anticipation of the future technological transitions. Besides intensively studied chemical systems and specific structural types (perovskite-related compounds for instance that cover almost all fields of applications of inorganic materials), one key-solution involves original structural types with unexpected specificities in unexplored chemical systems. This thesis will concern the synthesis and full characterization of such oxides with exotic mixed valence states, likely for redox-modification by controlled reaction. The work will cover synthesis and crystal growth, structural analyzes (X-ray and neutron diffraction), spectroscopic/thermal/electronic/magnetic characterizations and theoretical calculations and other more specified in-situ tests, depending on the concerned samples. Especially dealing with the elaboration methods, they will be various including solid state synthesis, solvo-thermal routes, high pressure, topotactic alterations … etc, well mastered by the two host-laboratories.

An international cotutelle position: This work will be shared between two universities (Unité de Catalyse et Chimie du Solide/ Univ. Lille-France and Institut für Anorganische Chemie/ Univ. Bonn-Germany) under the co- supervision of Dr. **Olivier Mentré** and Pr. **Robert Glaum**). They are both experts in Solid State Chemistry with complementarily fields of expertise. Among them, it is worth noting at the german-side the international leadership dealing with one efficient crystal growth technique by chemical vapor transport (2), see Fig.1a. ***To our experience, such a co-tutelle PhD-thesis is a unique experience and the most efficient way for a motivated student to acquire a broad expertise and a top-level solid-state-chemist background combining international specificities of two recognized laboratories, opening a wide range of opportunities for academic and industrial careers.***

Research Strategy: Transition metal (T) oxides allow a large versatility concerning the modification of the anionic lattice and the T redox. It allows generating new materials with various potentialities in crucial areas like energy, optics, magnetism, electronic-ionic transport, catalytic properties. Indeed, the mixed-valent vanadium phases develop very unusual phenomena such as orbital, charge ordering or metal-insulator transitions (3-4) but also stand at strategic positions for Li or Na intercalation batteries, catalysis and much more. Here the possible substitution of Ti^{3+} (d^1) by V^{3+} (d^2) with distinct d filling and spins suggests very specific and sizeable electronic features Fig.1b. Finally a rapid search in the literature highlights the unexplored crystal-chemistry of such systems adding covalent phosphates groups playing the role of building units toward various structural frameworks. Those systems will be explored using a rational "design"-like strategy. Concerning the targeted crystallographic structures, this work will be inspired by existing compounds of most "standard" chemical systems, or "inorganic-blocks" (Fig.1c) bringing their own specificities while assembled together. It is clear that a number of original compounds and properties will emerge from this thesis.

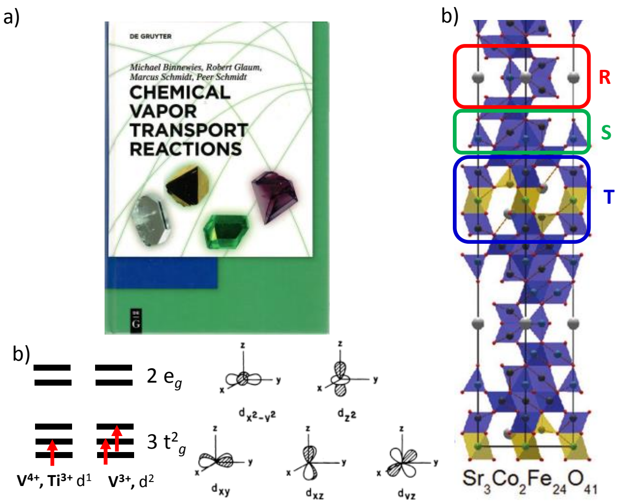

Figure 1: a) A book on CVT by R. Glaum et al. b) Magnetic electrons for Ti^{3+}/V^{3+}/V^{4+} ions in octahedral fields. c) Slicing of an inorganic structure in individual building units.

References: (1) R. Cava *et al.* Progress in Solid State Chem. (2002), 30 1. (2) R. Glaum *et al.* Chemical Vapor Transport Reactions, (2012), de Gruyter. (3) Y. Ueda *et al.* Solid State Sciences (2005), 7, 874. (4) Y.Junki *et al.* (2011) Journal of the Physical Society of Japan. (2011) 80, 073711.