



Sintering of oxides at the nano-scale : 3D environmental studies of the microstructure engineering of vanadate-based nanophosphors

Elaboration of well controlled colloidal nanoparticles is the subject of intense investigations focusing the appropriate control of the parameters affecting their property, such as composition, crystallinity, size, and morphology. Oxide nanoparticles with 30 – 150 nm often exhibit complex microstructures arising from nonclassical nucleation/growth processes (Fig. 1, left). We recently showed it possible to significantly orient the microstructure of YVO₄ nanoparticles by playing on experimental conditions [Neouze2020], but the physical properties of particles made at low temperature appear as altered due to detrimental effects of surface states or large amounts of punctual defects. A method for improving the crystallinity and remove defects is to achieve post-synthesis thermal treatments allowing for the annealing of the particles removing most internal porosity and defects [Mialon 2009, Maurin2013]. Interestingly, some annealing conditions resulted in perfectly crystalline nanocrystals, some of which exhibiting a **very original hollow nanostructure** (Fig. 1, right). Such structures are similar to those observed as a result of the so-called Kirkendall effect or galvanic replacement reactions [Chee2017], except that it seems to result from the pore evolution, *i.e.*, pore shrinkage resulting from surface diffusion and grain boundary diffusion.



Figure 1: Annealing of an YVO₄ nanoparticles leading to facetted monocrystalline nanocrystals, some of which presenting pores as a result of the densification process through sintering and crystal reconstruction.

The main objective of the present project is to answer the following scientific questions: i) Can we follow the thermal evolution of the microstructure with *in situ* TEM?; ii) What is the influence of external environment (gas, pressure, flux)? iii) Can we model the phenomenon? Iv) Can we engineer the nanostructure through playing on the pristine particles structure or on primary particles assembly? Significant part of the project will be devoted to synthesis and the structural characterisations, with transmission in-situ TEM for monitoring the structural evolution of various YVO₄ nanocrystals. This unique tool will enable in-depth analysis of morphological, structural, and chemical information during the thermal reconstruction under high temperature annealing. The nanoscale behaviour of the vanadate nanoparticles will be analysed in parallel with optical information arising from lanthanide spectroscopy and with the ensemble-like structural properties observed in laboratory conditions to design functional materials for new emerging applications in thermometry, chemical sensing, and catalysis.

Candidate profile and application process: The candidate has a PhD in materials chemistry with a background on nanoparticles synthesis or nanoceramics and TEM characterization. Application should be made by sending a CV and 2 letters of recommendation to Thierry Gacoin, Project coordinator (<u>thierry.gacoin@polytechnique.edu</u>). Online meeting can be organized if needed for more information before application.

Starting date : The position is opened for 1 year starting fall 2023, with possible extension of at least one year.

Research location and Collaborations : This work will be achieved in the <u>solid state chemistry group of the LPMC</u> <u>laboratory</u> under the supervision of Prof. T. Gacoin. Collaborations will involve the 3D-NanoREV consortium funded by <u>ANR</u> and <u>FAPESP</u> that includes the electron microscopy facility in Ecole Polytechnique (CIMEX), the group of E. Leroy (TEM tomography), the group of M. Plapp in LPMC (modelization), and the group of prof. Paulo Cesar de Sousa Filho at the department of inorganic chemistry of the University of Campinas, Brazil.

Literature and other information can be found at the following <u>link</u>.