Ecole Doctorale des Sciences Fondamentales

Title of the thesis: Fluoride nanoparticles synthesis by cold plasma process for application in energy

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Summary :
In the context of the acquisition of a new plasma reactor using fluorine, the Materials and Plasmas Processes group proposes to develop the synthesis of fluoride nanoparticles with controlled optoelectronic properties for applications in the field of energy. This thesis is indicated as a priority by the ICCF.

The synthesis of nano-materials has been of interest to the scientific community for many years. The interest of these nanoparticles arises, on the one hand, from their particular properties due to their size and morphology, and on the other hand, to the possibility of obtaining multifunctional composite as nanoparticles in a material matrix. To synthesize them, cold plasma processes are perfectly suitable: production of crystallized nanoparticles of high purity and at relatively low temperatures, original structures obtained without thermodynamic equilibrium and process eco-efficient (without solvents) and widely used in the industry[i]. These processes have made it possible to produce nanoparticles of many metals and oxides[ii], but far fewer studies are interested in fluorides whereas these materials exhibit extremely interesting properties in optics, magnetism, photocatalysis, electrochemistry… The objective of this thesis is therefore to understand and control the synthesis of fluoride nanoparticles by plasma process.

In this context, the use of the new deposition reactor will enable to synthesis a broad panel of fluorides by sputtering various targets in atmosphere with fluorinated reactive gas. First, the PhD student will explore different process parameters allowing the control of chemical composition, crystalline or amorphous nature of the nanoparticles, as well as their size and morphology, thus tuning their properties. In particular, the pressure in the chamber will play a role in clusters aggregation in the gas phase. And the electronegativity of fluoride should help trap these clusters in the plasma phase, favoring their growth. Understanding the mechanisms of nanoparticles formation will be based on the reactive sputtering expertise of the Materials and Plasmas Processes group. Thus, the plasma will be particularly studied, especially by Optical Emission Spectroscopy. The reactivity of fluorinated species would be understood through reactive sputtering models used in the group.

In the second phase, the PhD student will investigate the nano-architecture of these particles, which can be obtained, according to the conditions, as nanocrystalline

film, weakly agglomerated particles, inserted or not in a matrix, or isolated within an ionic liquid[iii]. For nanoparticles analysis, he will benefit from the wide range of characterization techniques available at the ICCF or via already established academic collaborations. Their composition and structure will be followed by X-ray diffraction, IR and Raman spectroscopies, Rutherford Retrodiffusion Spectrometry (CEHMTI in Orléans); their size distribution will be observed by electron microscopy. Finally, the optical properties necessary for applications in the field of energy will be investigated, among other things, by spectroscopic ellipsometry.

The candidate should have a Master degree in Materials Science or Materials Chemistry. A first experience in plasma processes and / or nanomaterials would be an asset. The candidate should be dynamic, autonomous and have a strong motivation in order to explore the various aspects of this project (plasma process, material carcterization, optical properties), but also should know how to work in a team. To apply to this proposal, please send to short CV, a motivation letter, yours marks in Master degree and a recommendation letter from your current supervisor. Moreover, an average of at least 14/20 in Master 2 is required for this prioritory proposal.

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[i] Chem. Rev. 2016, 116, 11061-11127.
[ii] Appl. Phys. A 2001, 73, 67-73.
[iii] Langmuir 2015, 31, 4323-4329.

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