AAP China Scholarship Council - CSC 2023

PROJET DE RECHERCHE DOCTORALE (PRD)

Titre du PRD : Ionic exchange of transition elements in glasses and glass-ceramics

DIRECTION de THESE

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Nombre de doctorants actuellement encadrés : 1

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Ecole doctorale de rattachement : Sélectionner

Nombre de doctorants actuellement encadrés :

CO-TUTELLE INTERNATIONALE envisagée : ☐ OUI ☒ NON

DESCRIPTIF du PRD :

*Ce texte sera affiché en ligne à destination des candidates et candidats chinois : il ne doit pas excéder **2 pages** doit être rédigé en **ANGLAIS***

Ionic exchange of transition elements in glasses and glass-ceramics

Introduction:

The ion-exchange (IOX) process usually consists in substituting alkali ions in a glass matrix by other ions coming from a molten salt bath into which the glass is immersed [1]. Ion exchange has mainly be considered for strengthening ($Na^+ \leftrightarrow K^+$) or for optical properties based on Cu or Ag nanoparticles (e.g. to produce waveguide sensors based on the surface plasmon resonance) [2]. The IOX process was largely used in the elaboration of stained glass windows. Indeed, from the beginning of the 14th centuries, the yellow coloration was obtained by IOX of silver and the precipitation of Ag nanoparticules. Nowadays, the technique of coating a glass with a metal-base precursor is still used but remains limited mostly to silver. The development of coloration with other transition (TM) or metallic elements could avoid the coloration in the bulk of the glass, which is often costly in industrial furnaces, and allow a better control of the redox process. Rare studies have demonstrated the possibility of IOX with other TMs such as Ni, Cr [3],[4]. The purpose of this project is to further explore this new doping route with TMs using IOX.

Moreover, in the past few years, IOX in glass-ceramics (GCs) has gained a considerable interest with a lot of research and new developments in academic and industrial labs [5],[6]. The ability to obtain outstanding mechanical properties with new IOX GCs has led to recent important commercial release for front or back covers of hand-held displays and tablets [2]. As a much wider range of properties can be tune in GCs compared to glasses, further developments considering transition metals (TMs) doping should open new perspectives for applications of high economic impact in many fields. For instance, we foreseen novel GCs for localized or oriented crystallization, reshaping of nanocrystals (IOX can modify the crystallization sequence or the crystal surface doping), or for patterning, with high potential for new optical active devices [7].

Here we propose an experimental research project to obtain glasses doped with TMs using IOX and to gain a comprehensive understanding of the material structure and microstructure. This rises challenging issues in order to answer outstanding questions: how important for controlling crystal nucleation is the glass composition and structure? What are the structural characteristics of the TMs sites obtained by IOX? how ion-exchange modifies the local structure, microstructure or crystal phase/composition in glass-ceramics?

Research plan:

Year 1: The first step of this project will rely on the $(Cu,Ag)^+ \leftrightarrow Na^+$ ion-exchange that is largely used for doping surface layers of glass [2]. Part of this study will be also dedicated to the study of ancient stained glass windows. Glasses will be based on ancient glass compositions and on the (Zn,Mg)O-Al_2O_3-SiO_2 system, which has been largely studied in PALM group. We will determine how the exchange layer is affected by glass composition (Na^+ vs K^+ vs Zn^{2+}). Composition and microstructural analysis will be used (SIMS; atom probe tomography; electron microscopy developed at IMPMC) to provide us a detailed understanding of the exchange mechanism.

Year 2: Based on the knowledge acquired in the first year, the student will then develop the IOX approach for TMs that are of attractive interest for luminescence/fluorescence properties but were rarely investigated (Ni, Mn, Cr). The second step of this study will determine how IOX modifies the crystallization sequence or how crystal doping at the surface of the nanophases (core-shell effects) can be controlled. Indeed, IOX in GCs is more complex than in glasses since it can occur in the residual glass, in the crystalline phases or at the crystal/glass interface and may modify the crystalline phase (amorphization, structural transformation) [8]. This investigation will be achieved using in-house facilities including XRD, TEM, Raman and optical spectroscopies.

Year 3: IOX can induce a compressive surface layer that is considered to modify the local environment. This hypothesis will be further explore using x-ray absorption spectroscopy (SOLEIL synchrotron) or optical spectroscopy measurements to determine how the TMs sites are affected by IOX. Such detailed atomic-scale observations have been scarcely investigated in IOX processes [9] and this will deliver fundamental understanding on the structural reorganization occurring during the atomic exchange.The results obtained in Years 1 and 2 will allow to focus the study on a given TM for which the IOX process is successful in order to develop gGCs with innovative optical properties such as modulated or persistence luminescence.

Year 4: The student will pursue the investigation started in years 2 & 3, mainly using synchrotron facilities. This could allow to develop disordered plasmonic systems with innovative properties.During this last year, the student will write articles and the manuscript of his/her PhD thesis.

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