



PhD thesis - University of Rennes: Material Sciences

Institute of Chemical Sciences of Rennes ISCR - Glasses and Ceramics Team.

Crystallization of chalcogenide glasses: towards new infrared transparent ceramics.

Background and objectives of the study:

Transparent ceramics are emerging materials in the field of photonics because of their wide range of applications: laser materials, scintillators, transparent shielding or optical lenses [1]. These materials generally have a cubic crystal structure (no birefringence) and are often obtained by pressing nanometric powders in order to limit light scattering and improve their mechanical properties. The development of new transparent ceramics is restricted by this process because it requires the development and the use of high purity nanometric ceramic powders. Moreover, the transparency of the ceramics obtained is often limited by the presence of residual porosity and/or the presence of secondary phases [1].

Recently, transparent ceramics have been developed by complete crystallization of oxide glasses such as aluminates, gallates, silicates or tellurites [2]. A key step of this process is to obtain a glass with the same chemical composition as the desired ceramic. The production of this glass by melt-quenching allows to obtain a dense material (free of porosity). An adequate thermal crystallization treatment allows to convert this glass into a polycrystalline and transparent ceramic [2].

The objective of this thesis will be to develop, by complete crystallization of glasses, new transparent chalcogenide ceramics with remarkable optical properties in the infrared. The potential applications of these materials concern thermal imaging for the medical field (diagnostics), quality control (detection of pollutants, thermal losses), automotive (night driving assistance), or security and defense (night vision).

It will be necessary to transpose and adapt this crystallization process to chalcogenide materials (non-oxide materials based on sulfur, selenium or tellurium). Based on the existing literature and the skills of the research team in Rennes (strong experience in the synthesis of "exotic" glasses), several chemical compositions will have to be identified and selected in order to test their ability to form a glass. These glasses will then be crystallized via an adapted thermal treatment to obtain ceramics. Different physico-chemical characterizations (XRD, DSC, TEM, EDS, optical...) will be performed to study these different materials. This work will focus on the structural characterization of the ceramic materials obtained: nature and morphology of the crystals, grain boundaries, possible residual phases... Within the framework of already well-established collaborations, in-situ structural characterizations could be carried out (XRD, SEM, HRTEM). The study of microstructure/transparency correlations during the crystallization process will then allow the optimization of the synthesis parameters (composition, annealing conditions...). Depending on the candidate's profile, spectroscopy (NMR, Raman....) could be used to deepen the study of the structure of these new materials. Finally, the transparent ceramics obtained will be characterized optically (transparency, luminescence) and mechanically.

This PhD position is part of a french ANR project entitled Chatofor "Complete crystallization of CHAlcogenide glasses: TOwards transparent ceramics FOR infrared applications." This project brings together two partners: the ISCR (Rennes) and the CEMHTI (Orléans) partners which have respectively recognized skills in the elaboration of non-conventional glasses (chalcogenide materials) and the characterization of crystallization





mechanisms of glass with specific structural tools. This experimental thesis work will allow the candidate to acquire expertise in the field of transparent ceramics, materials with emerging optical properties.

Location: Institute of Chemical Sciences of Rennes (ISCR) - 35042 Rennes Glasses and Ceramics team (https://iscr.univ-rennes.fr/glasses-and-ceramics-vc)

Funding: ANR PRC 2023 Chatofor

Doctorate school: S3M, Science de la Matière, des Molécules et Matériaux

Candidate profile: Master in Chemistry or Materials Science and Engineering. Research internship in the field of solid state/materials chemistry. Motivated and curious person.

Duration: 3 years (36 months)

Salary: ≈ 1600€ per month (net salary)

Starting date: September-December 2024

Supervisors:

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^[2] I. Milisavljevic, et al., Crystallization of glass materials into transparent optical ceramics. International Materials Reviews, 2022: 1-29.