# Standard Project

*Experimental Report*

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| **Proposal title:** Quantum dots crystallization through non-conventional process in amorphous oxide polycationic materials elaborated through sol-gel process. A joint SAXS and WAXS in-situ experiment | | **Proposal number: 20171079** |
| **Beamline: BM02** | **Date(s) of experiment:** From 2017, April 4th to 9th | **Date of report: Oct., 2018** |
| **Shifts: 15** | **Local contact(s):** Isabelle Morfin | ***Date of submission:*** |

**Objective & expected results:**

Dispersion of semiconductor oxide nanocrystals into glasses can result of heterogeneous crystallization process promoted by thermal treatment into bulk materials elaborated through the sol-gel process. In such a case the amorphous oxide materials are very far from the thermodynamic equilibrium and the crystallization usually occurs at temperature highly lower than that one observed in classical glass devitrification process. We have shown that such process can be used for the elaboration of materials made of nanosized tin oxide crystals embedded into amorphous silica matrix [1, 2]. One of the tricky point associated to the formation of these nanocrystals is the interplay between amorphous phases separation and crystallization processes. Thanks to the use of a new wide angle 2D XPAD detector now available on the BM02 beamline, we were able to record simultaneously the Small Angle and Wide Angle X-ray Scattering signal (see fig. 1). Thus, the aim of this experiment was to follow simultaneously phase separation and $SnO_2$ crystallization through *in situ* SAXS-WAXS coupled measurements during convenient thermal treatments.

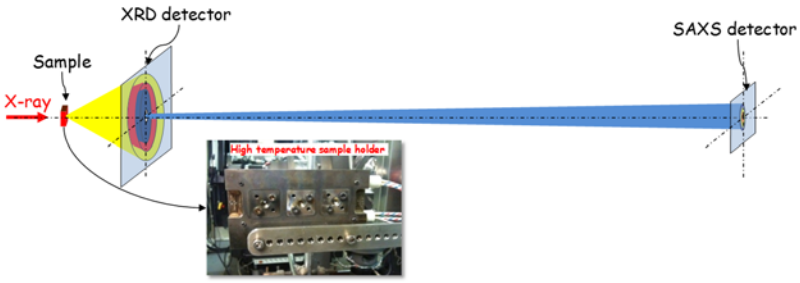


***Fig. 1. Layout of the experimental set-up.***

**Results and conclusions of the study:**

The energy of the beam was fixed at 24 keV (few keV below the tin absorption K-edge) and we have followed the evolution of SAXS and WAXS signals as a function of time and temperatures between 20 °C and 350 °C. Each SAXS or WAXS patterns were recorded both during 30 s.

As evidenced fig.2 through SAXS measurements whatever the temperature was, the pure silica matrix did not evolve. It means that thermal induced modifications of the SAXS signal recorded on mixed silicon and tin oxide xerogels are necessary related to the presence of tin.

The SAXS patterns recorded as a function of the temperature in the 170-190 °C range on a sample containing 10 at% of tin respect to silicon are reported fig. 3a. A crossover of the curves is clearly evidenced at 1.15 $nm^{-1}$. Increasing of the temperature induces an increase of the scattered signal in the high q region and simultaneously a decrease of this signal in the medium q-range. This behavior is certainly related to the formation of tin-rich areas, i.e. a phase separation process. The q-value of the crossover corresponds to a correlation length of $\xi$=5.5 nm that could be considered to be the mean distance of the tin-rich areas. Quantitative analysis of this observation is under way through modelling of the SAXS curves assuming a description of the xerogels microstructure as a

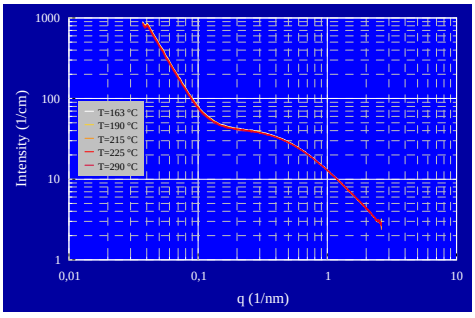


***Fig. 2. SAXS patterns recorded in situ as a function of the temperature for a pure silica xerogel.***

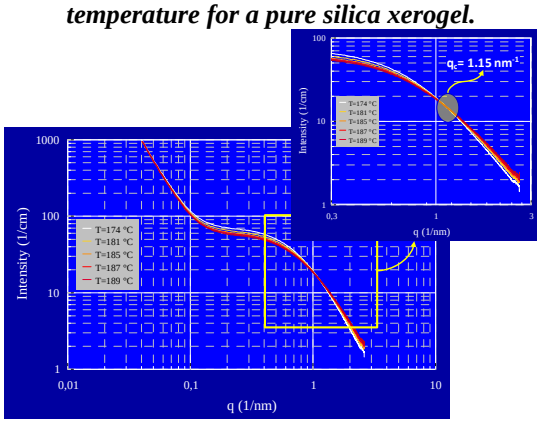


***Fig. 3. SAXS pattern recorded in situ as a function of the temperature for a xerogel containing 10 at% of tin.***

multiscaled fractal organization [3]. One of the preliminary quantitative results that we have obtained is a clear evolution of the fractal dimension into the xerogel that contains 10 at% of tin. In fact, this fractal dimension evolves from 2.4 to 1.9 when the temperature increases from 170 to 190. On the contrary, as we have written above, the microstructure of the pure silica xerogel did not evolved during the same temperature change. Moreover, the fractal dimension of these pure silica xerogel is equal to 1.9. It means that the phase separation process occurring during thermal treatment of the tin containing xerogels results on the formation of a matrix that is very similar to that one of the pure silica xerogels.

Long isothermal treatments induce the development of the phase separation process but they are also time consuming. We have recorded the SAXS and WAXS patterns on samples containing 4, 10 or 14 at% of tin during long thermal treatment at 190, 225, 315 and 350 °C. Some of the experimental results are reported on the fig. 4. It is worth to note that after 24 h of isothermal treatment at 190 °C the xerogel containing 10 at% of tin is still fully amorphous (see fig. 4a-grey line). The crystallization of tin oxide was followed at different temperatures between 300 and 350 °C. The evolution of the diffraction patterns recorded at 350 °C is reported fig. 4a. All the observed diffraction peaks are due to the presence of $SnO_2$ crystals into the cassiterite phase. The increase of the diffracted intensity is of course due to the increase of the volume amount of crystallized $SnO_2$ phase. One can see that it is associated to a clear decrease of the wide angle scattered signal. As we have shown previously [2], this effect is due to the decrease of the tin amount into the amorphous matrix. The XRD patterns were fitted using modelling process derived from the Rietveld approach. We have determined the evolution of the amount of both the cassiterite and tin located into the amorphous matrix and simultaneously the $SnO_2$ crystals mean size. In the case of the sample containing 10 at% of tin, after 9 hours at 350 °C, more than 50% of the introduced tin is under the $SnO_2$ crystals form. It seems that this amount is smaller for both the 4 and 14 at% containing samples. We have also checked the influence of the temperature and duration of the first thermal treatment that induces the phase separation process. It seems that a phase separation treatment at a low temperature promotes a high amount of cassiterite after the crystallization treatment.

Quantitative analysis of both the SAXS and WAXS patterns are one the way and a first presentation of the results of this experiment will be given during the "Matériaux 2018" congress in November 2018 in Strasbourg [4].

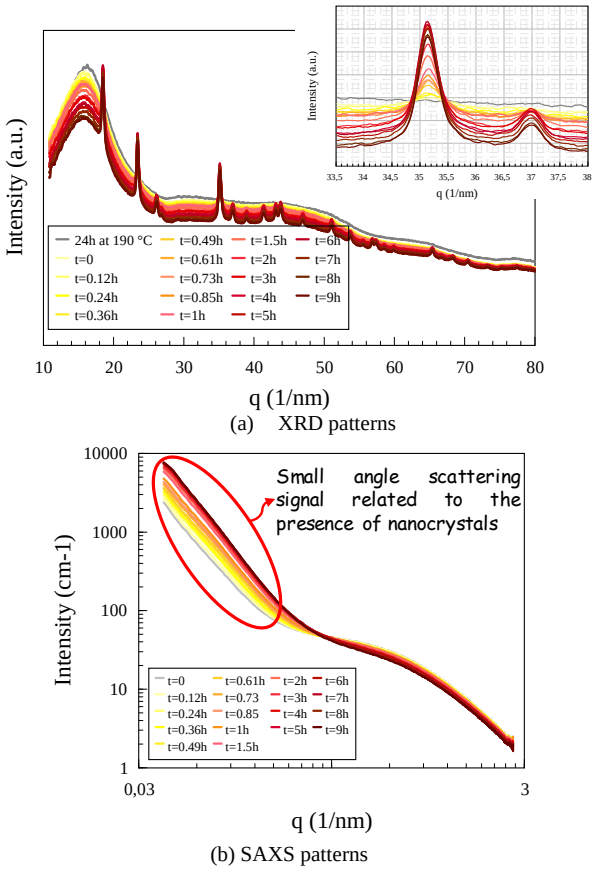


***Fig. 4. Microstructural evolution during isothermal treatment at 350 °C of a xerogel containing 10 at% of tin and previously heat-treated at 190 °C during 24 hours.***

**Justification and comment about use of beamtime**

Phase separation process and crystallization into polycationic xerogels are clearly two intricate phenomena occurring very far from the thermodynamic equilibrium. Consequently, only coupled *in situ* experiments are really able to shed light on such structural and microstructural evolutions occurring partially simultaneously. Thanks to new developments and the use of the set-up drawn fig. 1, the BM02 beamline is a unique experimental station very well adapted for such measurements.

**References**


[1] Y. C. Wu, W. Hamd, E. Thune, A. Boulle, C. Rochas, R. Guinebretière "*Synthesis of tin oxide nanosized crystals embedded in silica matrix through sol-gel process using alkoxide precursors*" J. Non-Cryst. Solids, 355 (2009) 951-959.

[2] B. Costille, M. Dumoulin, A.M. Ntsame Abagha, E. Thune, R. Guinebretière, "*Far from the equilibrium crystallization of oxide quantum dots in dried inorganic gels*" J.Phys. D: Appl.Phys. 51 (2018) 255303.

[3] M. Dumoulin, W. Hamd, E. Thune, C. Rochas, R. Guinebretière "*In situ time-resolved small-angle X-ray scattering observation of the fractal aggregation process in tin alkoxide polymeric solution*" J. Appl. Cryst. 49 (2016) 366-374.

[4] B. Costille, A. Bacouel, E. Thune, R. Guinebretière "*Mesures couplées de diffusion centrale et diffraction des rayons X in situ en fonction de la température sur la ligne BM02 à l'ESRF. Séparation de phases et cristallisation dans des matériaux inorganiques oxydes.*" Matériaux 2018, 19-23 nov. 2018, Strasbourg.