EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Thermally activated formation of nanoparticles in ionic glass matrix – novell glass-metal nanocomposites	**Experiment number**: HD-577
Beamline: ID02	**Date of experiment**: from: 13.06.2012 to: 15.06.2012	**Date of report**: 21.12.2012
Shifts: 6	**Local contact(s)**: Peter Boesecke	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Sindy Reibstein, *Anja Winterstein, *Daniel Schumacher, Guojun Gao, Lothar Wondraczek**

All: Friedrich-Alexander-University, Glass and Ceramics - Department of Materials Science; Martensstrasse 5; D – 91058 ERLANGEN

Now at

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Report:

Nanoparticle formation of Palladium, Gold and Silver in an ionic glass matrix of the sulfophosphate system SO_3-P_2O_5-ZnO-Na_2O was monitored by a combination of WAXS-SAXS experimental set up with the aim of directly observe nucleation, crystallization and crystal growth. The measurements combined ex-situ investigations of previously systematically prepared glass-metal nanocomposites of different thermal histories and investigations, where thermally activated nanoparticle formation was followed in-situ with the aim to describe the kinetics of particle formation and to derive informations for ionic motion in the respective glass matrix.

The dependency of Palladium solubility in x SO_3 - (38.01-x) P_2O_5 - 42.2 ZnO - 19.79 Na_2O (mol%) glass matrix was successfully described. It was found that Palladium solubility is decreased with increasing SO_3 content. This supports the idea of an increased tendency for particle formation in ionic sulfophosphate glasses. The ex-situ investigation of a previously heat treated Palladium doped glass series suggests Palladium operating as nucleating agent for matrix sulfate crystallization which seems to overlay particle formation.

In-situ investigations concentrated on thermal activated Silver nanoparticle formation in 19.11 SO_3 - 18.9 P_2O_5 - 42.2 ZnO - 19.79 Na_2O – 0.6 Ag_2O (mol%, nominal) glass. Nucleation and crystallization of metallic silver could be followed seperately from matrix crystallization events. Silver nanoparticle formation appears to be related to the structural relaxation around T_g ~ 290 °C. The activation energy of thermal activated silver nanoparticle formation was estimated from the combined WAXS-SAXS measurements to E_a = 175 kJ mol^{-1}. Porod analysis between 0.1 nm^{-1} < Q < 0.82 nm^{-1} indicates a non fractal system with a Porod slope of ~ -4, which is in consistance with a distinc heterogeneity of the original glass [1]. During particle formation with temperature Porod slope increases constantly indicating the development of fractal objects. Unfortunately matrix crystallization activation energy could not be quantified but seems to occur at lower temperatures than for undoped glass of the same basic composition. It must be noted that a serious amount of hydrated phosphate crystall phase ($Na_2(PO_3OH)$•$2(H_2O)$, Dorfmanite, ICSD 1289) was detected. This is attributed to the experimental requirement of having powedered sample for in-situ investigation which is not ideal for hygroscopic, surface crystallizing glasses.

Additional to the proposals program, some test measurements on glass samples in the systems xSrO-(1-2x)MnO- xB_2O_3, xSnO-(100 − x)P_2O_5 and vitreous SiO_2 with varying water content were carried out to evaluate the feasability of SAXS measurements on these glasses. Unfortuantely internal tensions, chemical heterogeneity of the glasses, or insufficient set up (to high Q-space) complicate the evaluation of the data. Therefore, special care should be taken on these issues regarding future proposals.

[1] S. Reibstein, N. Da, J.P. Simon, E. Spiecker, L. Wondraczek, *Phase separation and crystal precipitation in supercooled sulphophosphate ionic melts.* Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B 2012, Vol. 53 (3): S. 61-67.