	Experiment title: Redox and clustering of Manganese in Na-silicate glasses: a combined XAS and XEOL study.	**Experiment number**: MA-2537
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Report:
The preliminary data have been presented as oral contribution to the GOMD-DGG (Glass & Optical Materials Division and Deutsche Glastechnische Gesellschaft) Joint Annual Meeting 2015.

Sodium silicate glasses have been synthetised in air or under reducing conditions in order to characterize the speciation (local environment and oxidation state) of transition metal elements at low concentration.

The glasses compositions (Na-disilicate and Na-tetrasilicate) represent different glass polymerizations, thus the mobility of the dopant elements, expecially at ppm level, may be strongly influenced.

This first study was carried out with Mn as dopant element with concentration ranging from 5000 ppm to 100 ppm.

Preliminary informations on the glasses were collected with several lab-techniques, such as Raman spectroscopy, Optical Absorption and Luminescence spectroscopy, and EPR. Unfortunately with those techniques is very difficult to discriminate an accurate redox ratio and even more difficult is to derive unambiguous evidence on the element local environment. However, we have information on the distorsion of the site, and this info will be a perfect starting point for the EXAFS data analysis.

First of all we were able to acquire very good signal/noise ratio XANES and EXAFS signals. XAS spectra were acquired, at the Mn K-edge (6539 eV), in fluorescence mode by using a

multielements Ge detector. The Si311 monochromator ensured the resolution needed for the Mn pre-edge peaks analysis.

Four model compounds were analysed: MnO, MnO2, Mn2O3 and spessartine. They represent three different manganese valences and a different coordination environment (spessartine has Mn 8-fold coordinated). Moreover we collected, in transmission mode, two EXAFS spectra for a MnO pellet in order to derive an accurate S_0^2.

Mn foil was always collected simultaneously in transmission (reflexafs chamber) in order to have an internal calibration for each file.

We measured both bulk glasses and powdered samples and we tried to perform preliminary fast tests till the white line to see if photoreduction occurred. The fastest acquisition possible was 30 minutes and we detected slightly changes. Considering the signal/noise ratio for samples acquired as fast as possible and doped with 200ppm of Manganese, the observed variations of both pre-edge peak and white line, cannot be considered meaningful. But, for sure, this point is worth to be the subject of a future study.

In all the samples we detected the almost complete presence of divalent manganese, despite the color of the glasses varies significantly (from purple to colorless).

Neither the different glass polymerization, nor the manganese content, seem to influence the XANES signals. However, the EXAFS region revealed that some changes must occur, since we noticed a change in the frequency.

An average of 10 spectra in the EXAFS region were collected for samples with Mn <500ppm in order to have a good signal/noise ratio.

Further studies are needed since both optical absorption and luminescence spectroscopy, gave us different results. We were expecting to find matching and more accurate informations.