Standard Project

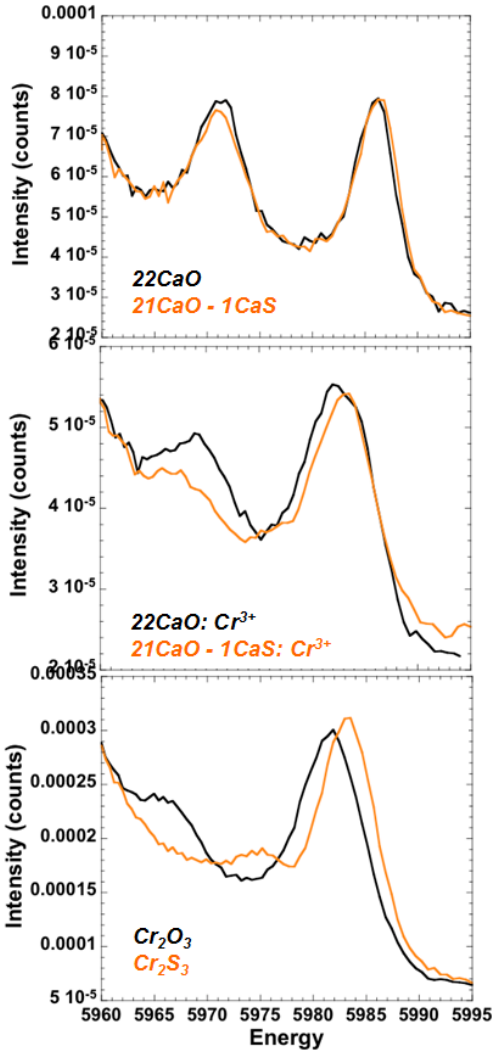
Experimental Report template

Proposal title: Cr local environment and ligand effect in glasses and glass-ceramics: a High Resolution XAS and XES approach		**Proposal number:** **20120969**
Beamline:FAME	**Date(s) of experiment:** from: 27/03/2013 to: 01/04/2013	**Date of report:** 12/07/2013
Shifts:18	**Local contact(s):Jean-Louis Hazemann**	*Date of submission:*

Objective & expected results (less than 10 lines):

We aimed at investigating the Cr local environment and to obtain information on the nature of its ligands in oxide, oxyfluoride and oxysulfide glasses and glass-ceramics. In oxide, oxysulfure, oxyfluorure glasses and glass-ceramics, Cr is thought to enter the sulfur/fluorine crystalline phase that forms upon heat treatment of the parent glass, conferring promising optical properties to the final glass-ceramic. It was thus highly desirable to determine Cr coordination and ligands in the parent-glass and in the final material to understand the relationship between the local structure and the optical properties.

We thus spent 6 days/18 shifts (2013 March 27th - April 1st) on FAME beamline to obtain information on Cr ligands and its electronic structure in these materials. We have performed Cr K-edge XAS under high resolution and valence-to-core XES. This latter spectroscopy investigates Kβ''/Kβ2,5 "valence-to-core" emissions, which stem from transitions from the filled ligand valence orbitals to the Cr 1s core hole[1,2]. XES is also a powerful technique in terms of identifying the chemical bonds around Cr, thus giving insight into the coordination[1,2].



Results and the conclusions of the study (main part):

The parents Cr-doped oxide, oxysulfide and oxyfluoride glasses were synthesized at IMPMC. We have investigated different glass compositions starting from (mol %) $45SiO_2$-$3Al_2O_3$-$30Na_2O$-$22CaO$-$0.5Cr_2O_3$ with CaO being progressively substituted either by CaF_2 or CaS.

To perform valence-to-core XES experiments, the FAME beamline set-up recently equipped with a high energy resolution five-crystal spectrometer for high quality fluorescence and absorption measurements was mandatory. We recorded the Kß'' and Kß2.5 satellites emission lines, whose energy position and depend on the type of ligand and on the metal-ligand distance.

The data we have obtained on FAME were of good quality and the signal to noise ratio was good given the low Cr content (0.5 mol% Cr_2O_3) and the intrinsic low intensity of the satellite lines analysed.

The preliminary analysis of the results show a change in intensity and position of the Kß'' and Kß2.5 satellites emission lines with the progressive substitution of CaO by CaS (figure). If we compare the spectra obtained on oxidized (Cr^{6+} and Cr^{3+}) and reduced (only Cr^{3+}) glasses with those of crystalline reference Cr_2O_3 and Cr_2S_3, we can clearly see an effect associated with the change in the nature of the ligands around Cr.

The experiments 20120969 on FAME beamline were successful. We managed to record high resolution Cr K-edge XANES spectra and Kß'' and Kß2.5 satellites emission lines on different parent glasses and glass-ceramics. We were able to detect changes on the local environment of Cr and its ligand as a function of the composition. The next step of this proposal would be to calculate the fine XES structures

of the valence-to-core XES using multiple scattering theory simulations, which could be done at IMPMC (Juhin et al.)[3]

Justification and comments about the use of beam time (5 lines max.):

The high resolution techniques available on FAME beamline allowed us to get valuable results that will help to understand the evolution of Cr structural environment in glasses and glass ceramics as a function of composition. These results are mandatory to understand the structural-dependent luminescence properties of such newly developed materials for telecommunications. In addition, the feasibility of the valence-to-core XES experiments performed on amorphous systems such as the investigated glasses opens up interesting possibilities for studies on glasses.

Publication(s):

(1) S. Eeckhout et al., J. Anal. At. Spectro., **2009**, 24, 215-223.
(2) I. Llorens et al., **2012**, Rev. Sci. Instr., 83, 6.
(3) A. Juhin et al., **2010** Phys. Rev. B., 78, 19.