



	Experiment title: Seeking silent species in cobalt-bearing colored glasses using HERFD-XAS, RIXS and XES: understanding the color and structure of glasses.	Experiment number: HD-629
Beamline: ID26	Date of experiment: from: 12.09.2012 to: 18.09.2012	Date of report: 15-01-2013
Shifts: 18	Local contact(s): Dr. Jean-Daniel Cafun	<i>Received at ESRF:</i>
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Report:

Transition metal (TM) ions induce most coloration processes in oxide glasses. Composition and manufacturing (thermal history) conditions deeply influence the local structure around the transition metal ions and thus glass color. The intense blue color of Co-doped silicate glasses is up to now interpreted as arising from tetrahedral Co(II) only. By coupling X-ray and optical absorption spectroscopies, we have recently shown the presence of 5- and 6- coordinated Co(II) in Co-doped oxide glasses, indicating a more complex Co(II) speciation than usually assumed. However, the contributions of each species superimpose in such a way that it is difficult to quantify their relative contributions using these spectroscopic approaches. The aim of this experiment was to get a direct approach of the relative contribution of the different Co(II) coordination states in glasses which is a key parameter to understand their colors. We used resonant inelastic X-ray scattering (RIXS), high-energy resolution fluorescence detected X-ray absorption (HERFD-XAS) and X-ray emission spectroscopies (XES) to study the effect of site symmetry and ligand nature on the Co(II) electronic structure in glasses with the comparison to crystalline references. Previously, various authors have used a combination of these techniques but this was the first attempt to apply them to Co(II) ions in oxide glasses.

Experimental details

We recorded HERFD-XAS spectra and 1s3p RIXS planes at the beamline ID26. The incident energy was tuned to the Co K-edge energy (7700-7720eV) with the Si(111) monochromator. The fluorescence emission was measured in the energy range of 1s1 3d8 → 3p5 3d8 decay ($K\beta$ main line : 7620-7680 eV). The satellite line spectra was recorded in the energy range of the $K\beta_{2,5}$ emission (7680-7720eV). The emitted energy was analyzed using a set of five Ge crystals (reflection <444>).

Experimental results

Figure 1 shows a comparison between the pre-edge region of the HERFD spectra for three crystalline references containing Co(II) with different site symmetries : ZnCoSiO_4 for tetrahedral Co(II) , $\text{Co}_3(\text{PO}_4)_2$ for five-fold Co(II) and $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ for octahedral Co(II). The differences in the pre-edge peak intensities and energy positions highlight the effect of the site symmetry on the Co(II) coordination sphere. The pre-edge peak corresponds to $1s \rightarrow 3d$ quadrupolar transition, which is parity-forbidden, resulting in a very weak intensity in octahedral symmetry. However, when changing to non-centrosymmetric symmetry, hybridation with 4p orbitals adds parity-allowed dipolar contribution to this transition, resulting in a significant increase of the intensity of the pre-edge peak.

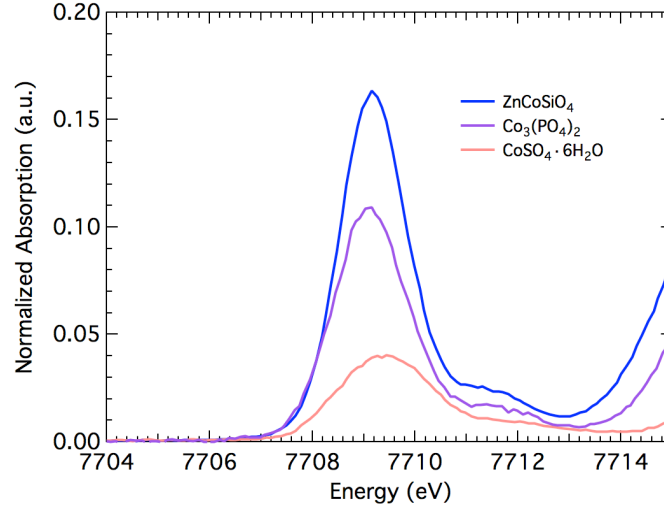
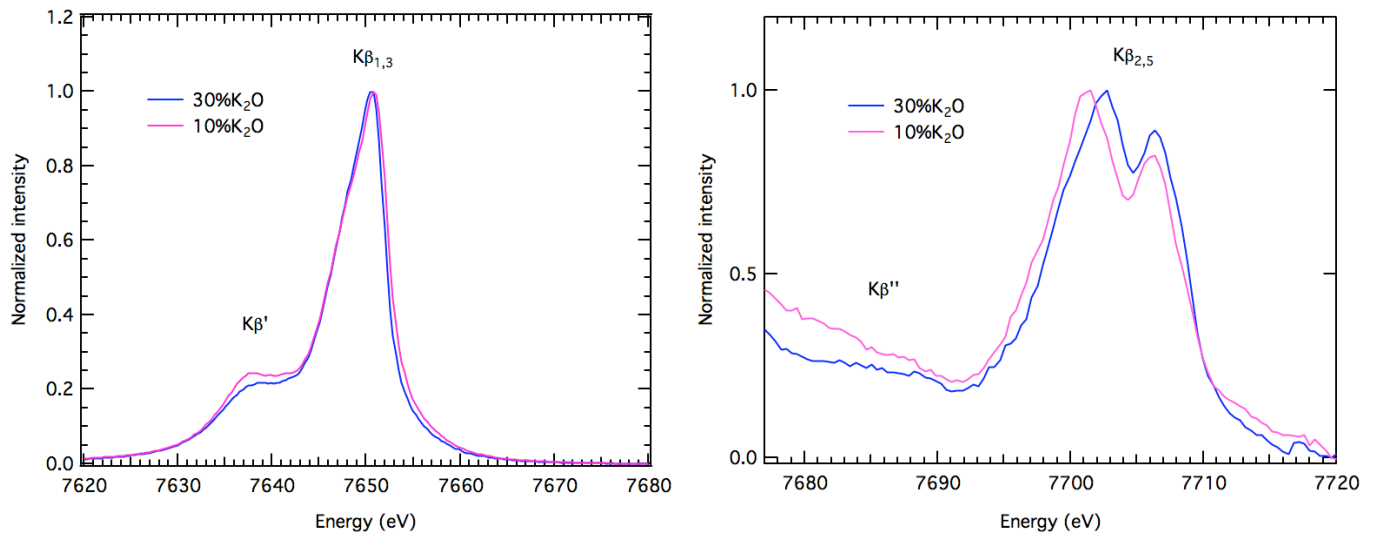


Figure 1. Normalized absorption HERFD spectra at the Co K-edge over the pre-edge region of ZnCoSiO_4 , $\text{Co}_3(\text{PO}_4)_2$, and $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$.

Figure 2 shows the X-ray emission spectra of two potassium borate glasses of different potassium contents. We observe that (Fig.2a) $\text{K}\beta_{1,3}$ shifts to lower energy and $\text{K}\beta'$ intensity is decreased when increasing potassium content; (Fig.2b) $\text{K}\beta_{2,5}$ and $\text{K}\beta''$ lines shift to higher energy upon increasing potassium content. The evolution of main lines evidences the modification of site symmetry with potassium content as previously revealed by optical absorption spectroscopy. Satellite lines reveal the change in the nature of the binding oxygen.



a) **b)**
Figure 2. Normalized XES spectra of two potassium borate glasses containing respectively 30% and 10% of K_2O . a) XES main lines corresponding to $1s3d8 \rightarrow 3p53d8$. b) XES satellite lines corresponding to $1s3d8 \rightarrow$ hole in valence orbitals.

Figures 3 a) and b) present the RIXS maps measured at Co K-edge of two reference compounds bearing Co(II) in tetrahedral and octahedral sites respectively. Figure 3 c) presents the first RIXS map at Co K-edge in silicate glass. The analysis of the emitted energy enables us to observe the presence of a second structure in the pre-edge region. Both structures are present on all the RIXS planes. However the difference of site symmetry modifies the shape, relative position and intensity of these two structures.

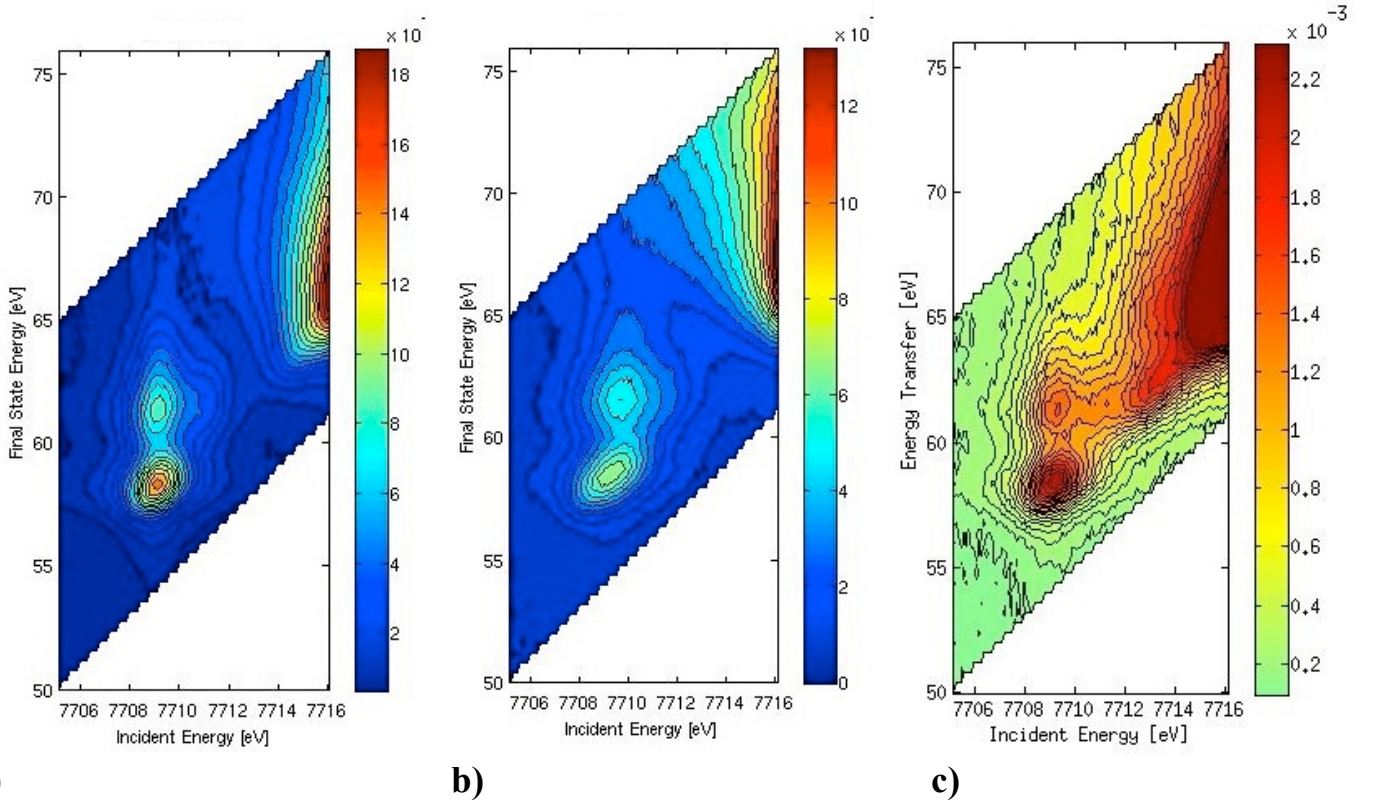


Figure 3. RIXS plane measured for : a) tetrahedral crystalline reference ZnCoSiO_4 , b) octahedral crystalline reference $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, c) Co(II) bearing silicate glass.

The present results show the effect of Co(II) coordination at the Co K-edge XANES over the pre-edge region and emission spectra. The experimental method of detecting the high energy resolution XANES spectra using an X-ray emission spectrometer gave us an opportunity to resolve the shape of the pre-edge transitions. Ligand field multiplet and TD-DFT calculations will enable us to further quantitative interpretations of these results.

Conclusions and further work

In this experiment, we have been able to study the speciation of Co(II) in reference compounds of wellknown crystalline structure with 3p-RIXS and XES techniques. It enables us to observe the effect of site symmetry on Co(II) electronic structure via 3p-RIXS planes and ligand nature via XES spectra. This will be used to identify the contribution of the different Co(II) species in glasses. Such high data quality was achieved thanks to the high resolution of both incident and emitted energies provided by the dedicated setup of ID26 beamline. These first experiments on transition metal ions in glasses encourage us to apply these techniques to the investigation of the structure-property relationship in glasses.