ESRF	**Experiment title: Investigation of the optical, electronic and structural properties of highly luminescent silver clusters confined in zeolite templates by X-ray Excited Optical Luminescence (XEOL) and XEOL-detected XAFS.**	**Experiment number**: **CH-4207**
Beamline: BM-08	**Date of experiment**: from: 27 Nov 2014 to: 03 Dec 2014	**Date of report**: 05/06/2014
Shifts: 18	**Local contact(s)**: Francesco D'Acapito	*Received at ESRF:*

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Report:

The main objective of our beamtime at BM-08 was to use X-ray Excited Optical Luminescence (XEOL)-detected XAFS to investigate the optical, electronic and structural properties of series of highly luminescent oligoatomic silver clusters confined in LTA and Faujasite zeolite scaffolds produced either by heat-treatment [1] or directly by X-ray irradiation.[2] XEOL-detected XAFS was expected to provide enhanced site selectivity and facilitate the determination of the structural and electronic properties of each type of luminescent clusters. The knowledge gained should provide us with a better understanding of the luminescence features of Ag-zeolite composites and contribute to the design of novel materials with optimized tailored properties for different applications.

Experimental

EXAFS data at the Ag K-edge (E = 25514 eV) of Ag-zeolite samples were collected simultaneously in transmission and XEOL-detection modes at GILDA beamline (BM08)[3] operating in a 24*8 + 1 mode with a current of 200 mA. The monochromator was equipped with a pair of Si (311) crystals and run in Dynamically Focusing mode. The harmonic rejection was carried out by using a pair of Pt-coated mirrors (Ecut off = 31 keV). X-ray Excited Optical Luminescence (XEOL) emission from the sample was collected by two lenses and sent, through an optic fiber, to a Photomultiplier Tube (PMT) (pulse duration <2ns) with sensitivity in the range (300–650) nm.[4] The samples were measured in ambient conditions as well as at liquid nitrogen temperature.

Two series of six Ag-LTA and six Ag-FAU heat-treated (activated) Ag-zeolite samples featuring different silver loading have been measured. Silver exchanged LTA samples were chosen for the dependence of their emission colors with respect to the silver content, whereas Ag-FAU materials were selected for their unusually high external quantum efficiencies reported up to 69 %.

Additionally we have also investigated the structural and electronic properties of luminescent Ag clusters formed directly under X-ray irradiation.[1] Two Ag-LTA and two Ag-FAU zeolites were measured in their non-activated (non-luminescent) states. In this case the Ag clusters were directly produced upon the X-ray irradiation during the XAFS measurements.

Although the relatively weak luminescence signal collected in this measurement mode produced a moderate signal-to-noise ratio in comparison to that of the transmission-detected EXAFS datasets, most of the time a reliable EXAFS signal could still be obtained up to k = 8 $Å^{-1}$ (Figure 1) at the cost of longer measurement times. Data analysis clearly showed that the structure determined from XEOL-detected data is significantly different from that obtained from conventional transmission-detected EXAFS. Combination of the structural models obtained with the two detection modes allowed us to fully characterise the structures of the luminescent species in Ag-exchanged zeolites demonstrating the potential of this technique to be applied to similar nanostructured luminescent systems.

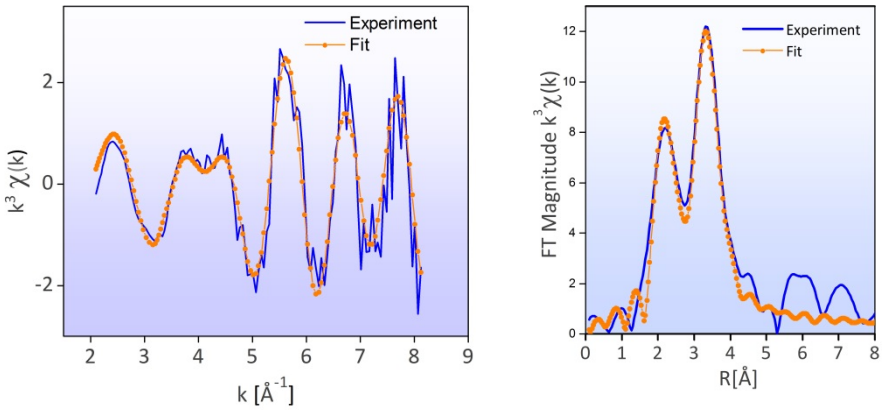

Figure 1. XEOL-detected Ag K-edge k^3-weighted EXAFS (left) with the corresponding phase corrected FT (right) best fits of heat-treated Ag_3K_9-LTA zeolite material.

A first publication is now in preparation where we describe for the first time the use of XEOL-detected EXAFS measured at the Ag-K edge to unravel the exact structure of the silver oligomeric clusters at the origin of the bright green luminescence observed in partially Ag-exchanged LTA zeolites that is one of the most challenging samples. We are currently finishing the analysis of the data of the Ag-FAU samples that should lead to a second contribution.

References

1. De Cremer, G.; Coutino-Gonzalez, E.; Roeffaers, M. B. J.; Moens, B.; Ollevier, J.; Van der Auweraer, M.; Schoonheydt, R.; Jacobs, P. A.; De Schryver, F. C.; Hofkens, J.; Baruah, M.; De Vos, D. E.; Sels, B. F.; Vosch, T., Characterization of fluorescence in heat-treated silver-exchanged zeolites. *J Am Chem Soc* **2009**, *131*, 3049-3056.
2. Coutino-Gonzalez, E.; Grandjean, D.; Roeffaers, M.; Kvashnina, K.; Fron, E.; Dieu, B.; De Cremer, G.; Lievens, P.; Sels, B.; Hofkens, J., X-ray irradiation-induced formation of luminescent silver clusters in nanoporous matrices. *Chem Commun* **2014**, *50* (11), 1350-1352.
3. D'Acapito, F.; Trapananti, A.; Torrengo, S.; Mobilio, S., X-ray Absorption Spectroscopy: the Italian beamline GILDA of the ESRF. *Notiziario Neutroni e Luce di Sincrotrone* **2014**, *19*, 1592-7822.
4. Fortes, L. M.; Goncalves, M. C.; Pereira, J. C.; D'Acapito, F., EXAFS study of Er,Yb doped hollow and dense SiO2 microspheres. *J Non-Cryst Solids* **2014**, *402*, 244-251.