ESRF	**Investigation of water-responsive luminescent metal clusters confined in LTA zeolite by X-ray Excited Optical Luminescence (XEOL) and XEOL-detected XAFS**	**Experiment number**: **CH-4818**
Beamline: BM08	**Date of experiment**: from: 16 Nov 2016 to: 22 Nov 2016	**Date of report**: 05/02/2017
Shifts: 18	**Local contact(s)**: Francesco D'Acapito	*Received at ESRF:*

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Report:

The goal of this proposal was to use X-ray Excited Optical Luminescence (XEOL)-detected XAFS to investigate the structure, environment and electronic properties of a series of novel highly luminescent oligoatomic lead and silver lithium /sulphur clusters confined in LTA zeolites as a function of the hydration state and metal and/or lithium loading. These clusters possessing very specific optical properties are generally formed during the controlled heat treatment under O_2/He gas flow of Ag/Li/Na/S and Pb exchanged LTA zeolites. Depending on the Li loading and the heat treatment temperature novel luminescent low Ag loading exchanged lithium-sodium-LTA zeolites can show emission from the green to the red. Heat-treated Pb-Na-LTA is a novel type of LTA zeolites containing lead clusters. These materials display a deep-blue emission with an external quantum efficiency (EQE) strongly depending on the lead content. Their emission colour and EQEs also show a strong dependence with respect to their hydration state. Finally, novel mixed AgS clusters in LTA zeolites present a remarkable white emission.

For this experiment we have recorded XAFS of various series of LTA zeolites at Ag K-edge (25514 eV) in XEOL-detection mode using a fast photomultiplier tube coupled to the sample via a condensing lens and an optic fiber available at BM08 and simultaneously in transmission mode. AgLiNa clusters within LTA zeolites corresponding to the formula $Ag_1(Li_xNa_{12-x})[Si_{12}Al_{12}O_{48}]$ were first investigated. A total of four Ag_1LiNa-LTA samples corresponding to Na pure (Ag_1Na_{12}-LTA); intermediate lithium loading ($Ag_1Li_4Na_8$-LTA) and full lithium loading (Ag_1Li_{12}-LTA) have been measured in pellets in their hydrated forms. High lithium loading dehydrated samples (Ag_1Li_{12}-LTA), ($Ag_1Li_{10}Na_2$-LTA) and ($Ag_1Li_{11}Na_1$-LTA) were measured in capillaries at LN temperature using the cryostat available at BM08. Dehydrated samples showed a marked loss of the

luminescence upon beam exposure suggesting a structural transformation of the clusters during the measurements

Two AgS-LTA samples were additionally measured in this beamtime. They also presented a marked degradation of their emissive properties during measurements.

Six Pb-exchanged LTA-zeolite (Pb_xNa_{12-x})[$Si_{12}Al_{12}O_{48}$] samples with different Pb loadings were also successfully measured at Pb L_3-edge (13035 eV). Low lead loading ($Pb_{0.5}Na_{11.5}$-LTA) and intermediate lead loading (Pb_4Na_8-LTA) samples dehydrated at 200 and 450 °C were successfully measured in capillaries while their hydrated forms were measured in pellets. A marked degradation of intermediate dehydrated samples was observed.

A total of 8 scans were generally collected for each sample to ensure a reasonable signal-to-noise ratio. Although the useful k range of the collected EXAFS is limited to kmax = 8 $Å^{-1}$ preliminary EXAFS analysis showed that the quality of the XEOL-detected data is likely sufficient to determine the structure of the luminescent clusters

The EXAFS data is curently being analysed. This investigation is expected to provide a better understanding of the relationship between the photo-luminescence properties and the structure, electronic properties and local environment of these Ag/Li, AgS and Pb clusters as a function of the metal content and the heat treatment temperature and contribute to designing novel materials with optimized tailored properties.