ESRF	**Experiment title:** X-ray absorption study of rare earth´s local structure in nanocrystalline glass-ceramic	**Experiment number**: 25-01-644
Beamline: BM25	**Date of experiment**: from: 1/3/08 to: 4/3/2008	**Date of report**: February 27th 2008
Shifts: 9	**Local contact(s)**: Dr. Iván Da Silva	*Received at ESRF:*

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Report:

Photonic devices based on rare earth (RE^{3+}) ions doped glasses and glass-ceramics are of special interest for the industry for their use in communication systems, such as fibers, optical amplifiers, high density optical data storage or infrared and visible solid-state lasers. The oxufluoride glass-ceramic studied, obtained after a thermal treatment of the precursor SiO_2-Al_2O_3-CdF_2-PbF_2 based glass, is a two-phase material that consists of a fluoride-type β-PbF_2 nanocrystalline phase embedded in an aluminosilicate glassy medium. In this temperature-induced process the rare earth ions are mainly incorporated in these nanocrystals, changing completely their physical properties. Optical measurements using the Eu^{3+} as a local probe ion has shown that the environments occupied by the optically active ions depend largely on the doping concentration, and at concentration of 2.5 mol% two distributions of local environments has been found. However, the exact local structures of the RE^{3+} ions are still unknown.

The aim of this work was to explore the local structures (bond distances and coordination numbers) of the rare earth ions RE^{3+} (Nd^{3+}, Eu^{3+} and Er^{3+}) and the Pb^{2+} ions in the precursor glasses and glass-ceramics for different concentrations and their influence in the optical properties of these matrices through the EXAFS measurements.

Studies were performed at the beamline BM25 at room temperature in transmission geometry. Alignment was carried out using the L_3-edge of a Re foil (10.535 KeV) as reference. Lot of problems were found with the optics alignment and, due to the bending effect, we finally decided to fix the pitch for the whole beamtime. Preliminary measurements showed that, in order to obtain sufficient statistical accuracy, a large number of absorption spectra should be added up. Thus, and due to lack of time, we decided to studied the absorption of the Eu^{3+} ion in detail measuring in the range from 6.85 to 7.4 KeV and with a typical total time of 1-2 hours per spectrum. As an example, up to 7 absorption spectra were add up for the glass sample doped with 1 mol% of Eu^{3+}, up to 10 for the glass-ceramic doped with 1 mol% of Eu^{3+} and 5 for the glass-ceramic doped with 2.5 mol% of Eu^{3+}. For the low doped samples (0.1 mol% of Eu^{3+}) different

measurements with large statistics were tried, but it was impossible to have a good signal and too much time would be needed to have a reasonable spectrum, so we decided not to perform these measurements.

Typical XANES/EXAFS spectra are shown in Fig. 1. Visual inspection of the absorption spectra clearly shows that only small differences are found in the XANES region. However, for the samples doped with 1 mol% of Eu^{3+}, the Fourier transform magnitude of the k-weighted $\chi(R)$ seems to indicate that while there is only one peak around 1.88 Å related to the mean distance from the Eu^{3+} to the nearest oxygen/fluor ions in the glass, there exists two peaks at 1.20 Å and 1.9 Å associated to two different Eu^{3+}-F^- coordination spheres in the β-PbF_2 nanocrystals. These results would confirm those obtained from laser spectroscopy techniques.

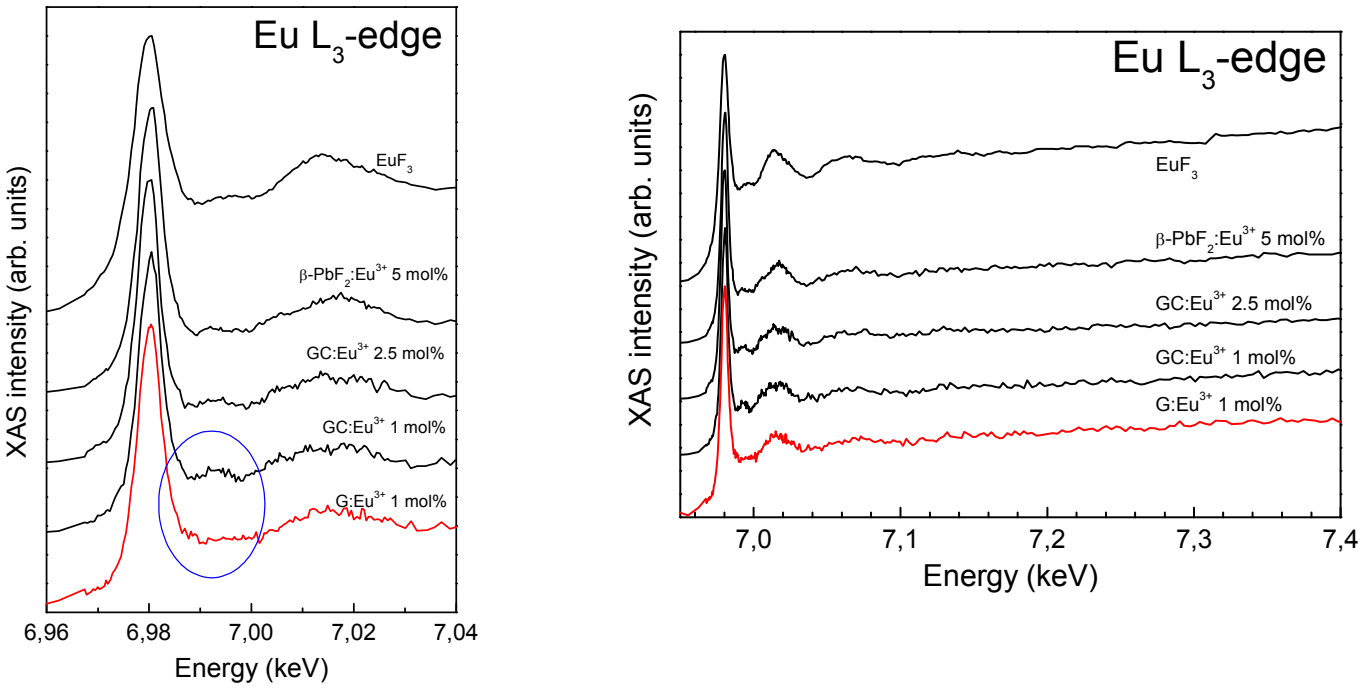

Figure 1. L_3-edge absorption spectra of Eu^{3+} ions in oxyfluoride glass (G) and glass-ceramic (GC) for different concentration of optically active ions. EXAFS spectra in β-PbF_2 and EuF_3 crystals are also included for comparison.

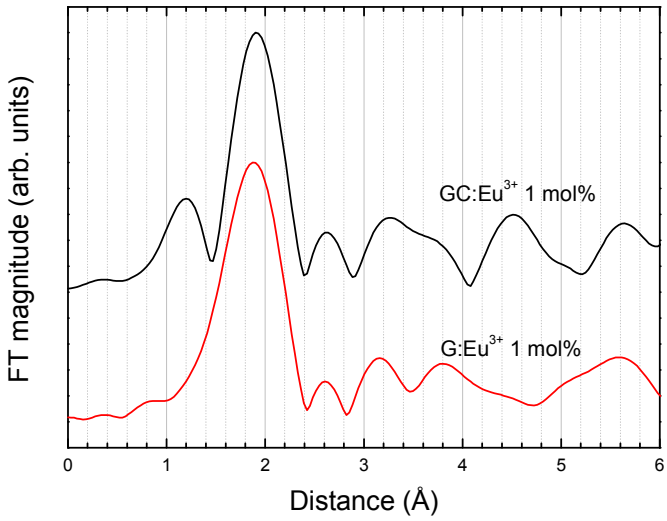

Figure 1. Fourier transform magnitude of the k-weighted $\chi(R)$ function.