	Experiment title: X-ray absorption study of rare earth´s local structure in transparent nanocrystalline glass-ceramics for photonic applications	**Experiment number**: HS3773
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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 1 mol% two distributions of local environments has been found in the glass-ceramic. 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 Tm^{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 BM29 at room temperature in transmission and fluorescence geometries, although the latter one was the only option for most of the samples due to the low concentration of RE^{3+} ions in these samples. Alignment was carried out using the L_3-edge of a Fe foil (7.112 KeV) as reference. We focus our experiments in Neodymium, Europium and Thulium RE^{3+} ions in order to analyze differences along the RE^{3+} series. Due to the small signal a typical measurement took between 20 to 30 s per point, whereas for the low doped samples (0.1 mol% of RE^{3+}) different measurements with even large statistics were tried.

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 for the glass and the glass-ceramic for the three RE^{3+} ions. However, for the samples doped with 1 mol% of Eu^{3+}, for which the EXAFS signal seems to be larger, the $|\chi(R)|$ shows that while there is only one peak around 1.85 Å related to the mean distance from the Eu^{3+} to the nearest oxygen/fluor ions in the glass, there exists two peaks at around 1.65 Å and 2.15 Å associated to two different Eu^{3+}-F^- coordination spheres in the β-PbF_2 nanocrystals. The similar spectra for the glass-ceramic and the β-PbF_2 crystals clearly states that both distributions of environments are located in the nanocrystals and would confirm those results obtained from laser spectroscopy techniques.
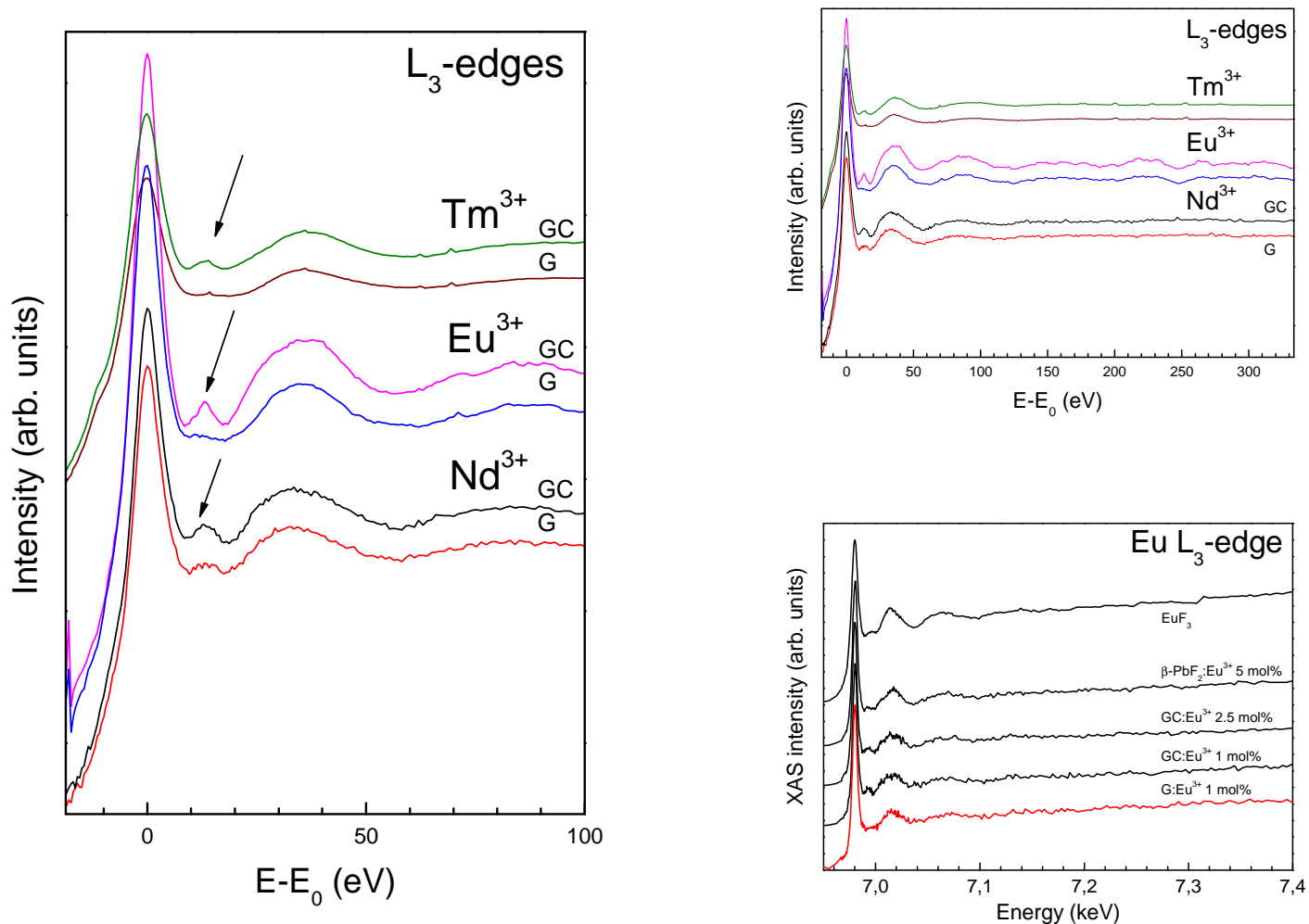
Figure 1. (Left) XANES spectra at the L_3 absorption edge of the Nd^{3+}, Eu^{3+} and Tm^{3+} ions in oxyfluoride glass (G) and glass-ceramic (GC) for 1 mol% of optically active ions. (Up-right) XAS spectra of Nd^{3+}, Eu^{3+} and Tm^{3+} ions. (Down-right) XAS spectra of the Eu^{3+} ions in for different concentration of optically active ions and in PbF_2 and EuF_3 crystals for comparison.
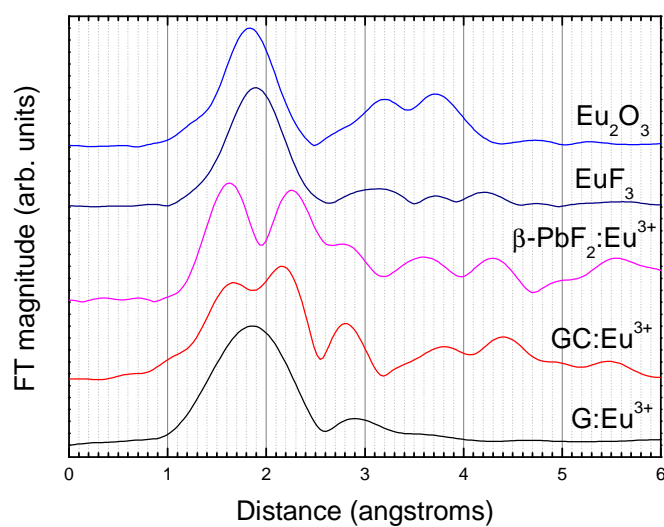

Figure 2. Fourier transform magnitude of the k-weighted $\chi(R)$ function for different samples doped with Eu^{3+}