



	<b>Experiment title:</b> EXAFS study of the local around Er <sup>3+</sup> ions in nanocrystalline tellurite-based glass ceramics	<b>Experiment number:</b> <b>08-01-311</b>
<b>Beamline:</b> BM08	<b>Date of experiment:</b> from: October 6 to: October 10	<b>Date of report:</b> July 2004
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Francesco D'ACAPITO (e-mail: dacapito@esrf.fr)	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Dr. Francesco D'ACAPITO*</b> <b>Prof. Rui M. ALMEIDA*</b> <b>Eng. Luis FORTES*</b> <b>Dr. Maria Clara GONCALVES*</b> <b>Dr. Luís F. SANTOS*</b>		

#### Report:

**This work is described in the following article: “Influence of Er<sup>3+</sup> on the early stages of crystallization of chloro-tellurite glasses studied by XRD and EXAFS”  
L.M. Fortes, L.F. Santos, M.C. Gonçalves, R.M. Almeida and F. D’Acapito  
(Accepted for publication in Journal of Non-Crystalline Solids)**

The purpose of this work was to study the local environment of erbium in Er<sup>3+</sup>-doped TeO<sub>2</sub>-ZnO-ZnCl<sub>2</sub> glasses. These glasses have a photoluminescence band near 1.53 μm, with a full width at half maximum larger than 60 nm, making them suitable potential materials for wavelength division multiplexing (DWDM) systems. Since the spectral broadening of the Er<sup>3+</sup> emission and the intensity of its luminescence is determined by its local environment, namely the symmetry and ligand field strength around it, extended X-ray absorption fine structure (EXAFS) spectroscopy was used to determine the Er<sup>3+</sup> near-neighbour environments in these oxyhalide glasses. The studied compositions were 40 TeO<sub>2</sub>-20 ZnO-40 ZnCl<sub>2</sub> (hereafter designated by 424) and 60 TeO<sub>2</sub>-20 ZnO-20 ZnCl<sub>2</sub>

(hereafter designated by 622) (expressed in mol %), doped with an additional x mol% of erbium (x=1 to 10), hereafter designated by 622+x.

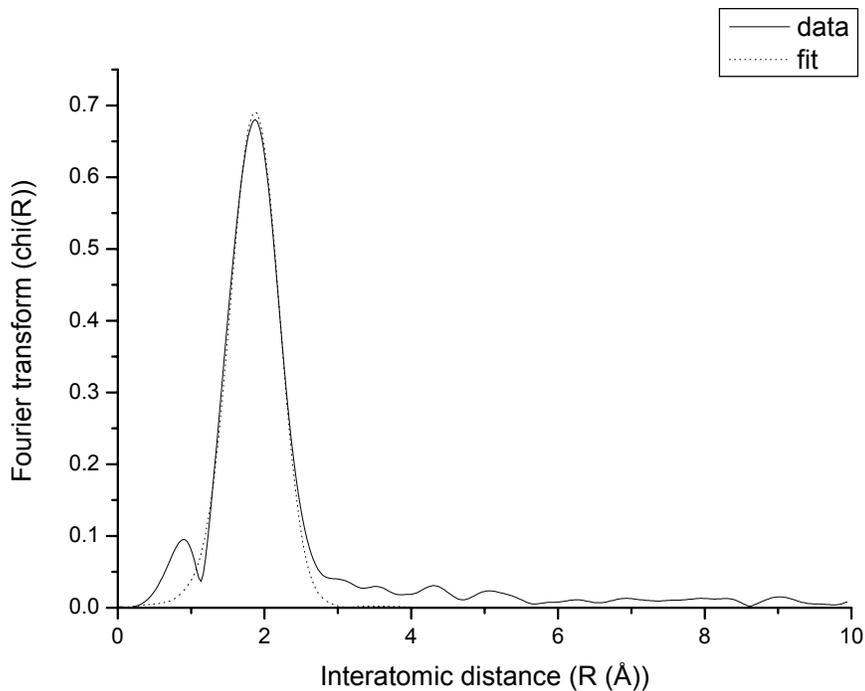
The EXAFS data were collected at the X-ray absorption spectroscopy hutch of GILDA (BM08 line), under the supervision of Dr. Francesco D'ACAPITO. EXAFS spectroscopy was carried out for glass plates, as a function of the glass composition, at the Er L<sub>III</sub> edge (8,358 eV), in the fluorescence mode, at 77 K. The spectra were collected in the range of 8300-9600 eV. The quantitative study was limited by Fourier Transform (FT) to the k-range of 2.05-10.5 Å<sup>-1</sup>. Since a rare-earth doping higher than 5 mol% could in principle induce some degree of self-absorption, fluorescence and transmission detection modes were recorded at the same time, in some cases. The results presented the same amplitudes within errors, even for samples with 10 mol% Er, showing no self-absorption effects. Data analysis was performed with the FEFF software package. The backscattering phase and amplitude data of the Er-O pairs were obtained from crystalline Er<sub>2</sub>O<sub>3</sub> data, using the *autobk* data extraction software and the *feffit* data fit.

The EXAFS results revealed an Er-O first coordination shell for all compositions. In fact, compositions with 0, 20 or 40 mol% ZnCl<sub>2</sub> always presented an Er first coordination shell similar to that of erbium oxide, with a coordination number equal to 9 (±1), at an average distance of 0.234 nm. Figures 1 and 2 present the Fourier transforms for the 622+2 and 622+10 glass compositions, revealing the oxygen affinity of erbium for both compositions.

Figure 2 illustrates the effect of heat-treatment: although the first coordination shell remained unchanged, the second coordination shell was more intense, which was also observed in the 424 glass composition, after heat treatment. Although this peak could not be unambiguously assigned at present, due to the lack of appropriate standards, the possibility of it corresponding to Er-Er interactions was discarded, based on the FEFF software, since it led to unacceptable fittings of the EXAFS data. The second peak changed with the heat treatment and the analyses performed suggest that this peak could be due to Er-Te interactions, which may be due to Er-O-Te bonding environments. In any case, the absence of Er-Er interactions indicates a homogeneous dispersion of the Er<sup>3+</sup> ions in the glass matrix.

EXAFS results showed that erbium was always surrounded by approximately nine oxygen atoms, with a typical bond length of 0.234 nm and no erbium-chlorine correlations were found. For heat treated samples, a distinct second near-neighbour peak was resolved, perhaps due to Er-O-Te bonding environments. The absence of close Er-Er interactions indicated a homogeneous distribution of the Er species in the material.

**Fig 1** – EXAFS modulus of the Fourier transform ( $\chi(R)$  amplitude) of the experimental data for glass 622+2 and theoretical fitting (not corrected for phase shifts), assuming nine oxygen atoms, at an average distance of 0.234 nm, as first neighbours of the central  $\text{Er}^{3+}$  ion.



**Fig 2** – Effect of heat treatment on the second near-neighbour peak of the Fourier transform (not corrected for phase shifts), for glass 622+10, before and after heat treatment at 410 °C for 1 hour.

