



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Structural study of rare earth environments in GeO₂-TeO₂-SiO₂-based glasses and glass-ceramics by XAS.

Experiment number:
HD-513

Beamline: BM08	Date of experiment: from: 02 June 2011 to: 07 June 2011	Date of report: 27/8/2013 <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): Dr. Francesco D'ACAPITO (e-mail: dacapito@esrf.fr)	

Names and affiliations of applicants (* indicates experimentalists):

Prof. Luís F. SANTOS* (Instituto Superior Tecnico, Departamento de Engenharia de Materiais Av Rovisco Pais - 1049-001 LISBOA).

Prof. Rui M. ALMEIDA (Instituto Superior Tecnico, Departamento de Engenharia de Materiais Av Rovisco Pais - 1049-001 LISBOA).

Dr. YIGANG LI* (Instituto Superior Tecnico, Departamento de Engenharia de Materiais Av Rovisco Pais - 1049-001 LISBOA).

Gonçalo MONTEIRO* (Instituto Superior Tecnico, Departamento de Engenharia de Materiais Av Rovisco Pais - 1049-001 LISBOA).

Dr. Francesco D'ACAPITO* (GILDA CRG -BM08 - ESRF 6 rue Jules Horowitz BP 220 F - 38043 GRENOBLE).

Report:

Resume

This work was presented in the International Symposium on Non-Oxide and New Optical Glasses, 1-5, July, 2012, Saint-Malo, France and is described in the following article:

G. Monteiro, L. F. Santos, R. M. Almeida and F. D'Acapito, "Local structure around Er³⁺ in GeO₂-TeO₂-Nb₂O₅-K₂O glasses and glass-ceramics", Journal of Non-Crystalline Solids, In Press, Corrected Proof, Available online 7 January 2013. Elsevier; <http://dx.doi.org/10.1016/j.jnoncrysol.2012.12.019>.

The purpose of this work was to study the local environment of erbium in Er³⁺-doped germanotellurite glasses and glass-ceramics in the (80-x) GeO₂-xTeO₂-10Nb₂O₅-10K₂O system (x=0-80 mol%). The heat treatments were performed based on differential scanning calorimetry data. Several crystalline phases, including α-TeO₂, δ-TeO₂ and GeO₂ (α-quartz), together with K[Nb_{1/2}TeO_{2/3}]2O_{4.8}, could be distinguished in the X-ray diffraction patterns. The 1.5 μm photoluminescence (PL) emission of Er³⁺ (4I^{13/2}→4I^{15/2}) has been studied in the glasses and glass-ceramics and the latter revealed a general increase in the bandwidth of the emission spectra, compared to the PL peak of the starting glass samples. Some heat treated compositions presented Stark splitting of the 4I^{13/2}→4I^{15/2} transition, indicating that the environment around the Er³⁺ ions had changed from an amorphous matrix to a more ordered environment. Therefore, Extended X-ray Absorption Fine Structure spectroscopy measurements were performed in order to investigate the Er³⁺ coordination shell before and after heat treatments. The glass compositions presented only one coordination shell around Er³⁺, composed of oxygen, while two coordination shells could be distinguished for the heat treated samples: a first oxygen coordination shell for all heat treated compositions and a mixed second nearest neighbor shell of Te and Er ions, for the Te-rich compositions (x=80 to 50), and of Ge and Er ions, for the Ge-rich compositions (x=10 and 20).

Experimental Conditions

EXAFS spectroscopy measurements were conducted at the X-ray absorption spectroscopy hutch of GILDA at the ESRF (European Synchrotron Radiation Facility). The heat treated glass samples were finely ground and

homogeneously dispersed in cellulose thin pellets with 13 mm diameter. The spectra were collected in the range of 8160-9250 eV to observe the Er-LIII edge (8358 eV) in the fluorescence mode at liquid nitrogen temperature (77K). The signal was collected from a 13-element high-purity Ge detector.

The EXAFS data were analyzed with the Ifeffit (version 1.2.11c) software package. First, with Athena GUI, the oscillating part $\chi(k)$ that contained the information on the local structure as a function of the photoelectron wave-vector k was extracted. This function was then analyzed with Artemis GUI, by fitting either in back-transformed space or in Fourier space the respective $\chi(k)$ or $\chi(R)$ function to a pre-defined crystallographic model (feff.dat file), in order to estimate the unknown parameters, the amplitude reduction factor (S_0^2), the mean square fluctuation of R (Debye–Waller factor, σ^2), the bond length in single scattering paths (R) and the number of neighbors (N).

Results and Discussion

The results from EXAFS measurements revealed a single coordination shell for all the glasses, which was attributed to the presence of oxygen atoms as first neighbours (Er-O) (Fig. 1a **Error! Reference source not found.**). The EXAFS spectra of the glasses also make it possible to conclude that no short range clustering of Er^{3+} ions occurred in these glasses, given that no second coordination shell was observed. The fittings were performed considering an Er_2O_3 standard crystalline phase (ICSD 27774).

EXAFS was also obtained for the heat treated compositions and it was found that Erbium forms two distinct local environments: a first coordination shell is present for all compositions and a second coordination shell throughout the germanotellurite glass-ceramic system studied: attributed to Ge for low tellurite content samples or attributed to Te for samples with more than 50 mol % of TeO_2 (Fig. 1b).

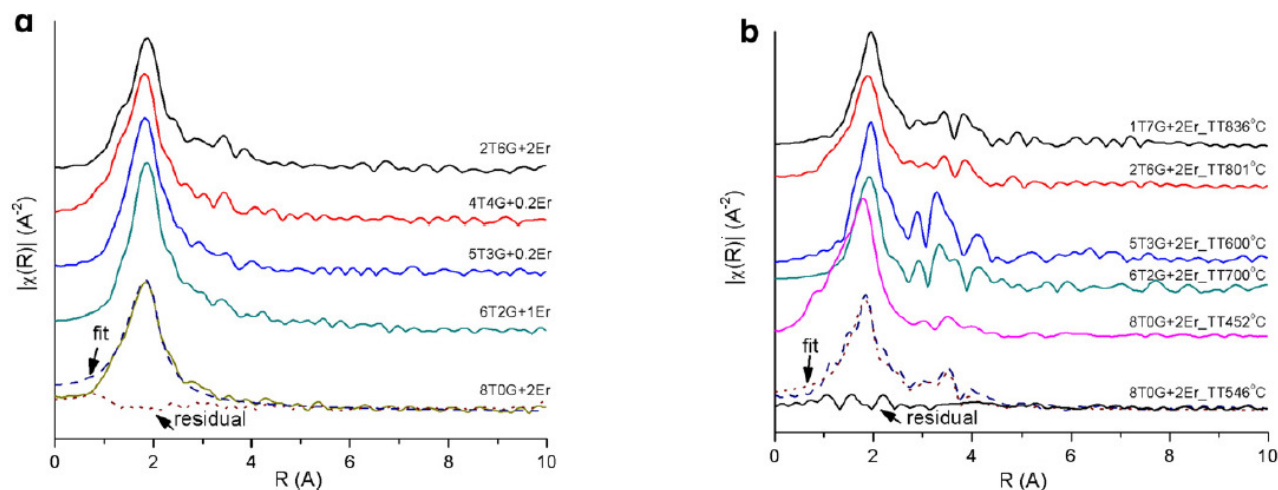


Fig. 1. a) $\chi(R)$ signals resulting from the Fourier Transform of the respective $\chi(k)$ signal, for the germanotellurite glasses and b) $\chi(R)$ signals resulting from the Fourier Transform of the respective $\chi(k)$ signal, for the glass-ceramics.

As an example, Table 1 presents the calculated coordination numbers, bond lengths and Debye Waller factors for the $8\text{T}0\text{G}+2\text{ErO}_{1.5}$ HT@546°C sample by fitting the EXAFS $\chi(k)$ signal to the $\text{Er}_2\text{Te}_5\text{O}_{13}$ crystalline structural data (ICSD 413666).

Glass-ceramic	Bond	Coordination number, N	bond length, (Å) (±0.02 Å)	Debye Waller factor, σ^2 (Å ²)
8T0G+2ErO _{1.5} HT@546°C	Er-O	7.2 ± 1.6	2.25-2.96	0.0044 ± 0.0028
	Er-Te	8.0 ± 1.8	3.79-3.99	0.0083 ± 0.0051
	Er-Er	3.6 ± 0.8	4.04-4.16	0.0035 ± 0.0099

Conclusions

EXAFS results indicate a first oxygen shell with a coordination number of 6.7 to 8.1, with an Er-O distance of 2.28 to 2.313 Å, for all glass compositions.

For heat treated samples, two coordination shells could be distinguished: a first oxygen shell for all the heat treated compositions and a second shell formed by Ge and Er ions for germanium-rich compositions or Te and Er ions for the 50–60% and 80% TeO₂-containing glass-ceramics.