



GILDA (ITALIAN BEAMLINE) ON BM8

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The Italian CRG beamline GILDA is financed by three major Italian public research institutes (Consiglio Nazionale delle Ricerche CNR, Istituto Nazionale per la Fisica della Materia INFN and Istituto Nazionale di Fisica Nucleare INFN). It has been operational since September 1994 and is mainly dedicated to the investigation of local structure. To this purpose, x-ray absorption spectroscopy as well as x-ray diffraction are used on the beamline in the energy range 5-50 keV.

The beamline GILDA consists of four experimental hutches. The first experimental hutch, in the 1:3 focal configuration which ensures the maximum flux, is dedicated to X-ray Absorption Spectroscopy (XAS). The wide energy range of the beamline makes GILDA well-suited for XAS investigations on heavy elements with the possibility to access the K absorption edges from Ti ($Z = 22$) to Eu ($Z = 63$). Experiments are carried out in transmission, fluorescence and total electron yield modes. For the study of highly diluted samples a 7-element high-purity Ge detector is currently used (current limit sensitivity: 10^{14} at/cm²). Surface experiments in total reflection mode (ReflEXAFS) are performed in a dedicated experimental chamber.

The second hutch, in 1:1 focal geometry, is dedicated to x-ray scattering and diffraction. It is equipped with a two-circle diffractometer with an angular step of 0.28 arcsec and a reproducibility of 2 arcsec. Crystal analyzers, solid-state detectors and scintillators are used to perform anomalous scattering on amorphous materials, and powder diffraction with an instrumental angular resolution lower than 0.01 degree. The installation of an Image Plate detector is foreseen. Anomalous x-ray reflectivity spectra have also been collected. Finally, Diffraction Anomalous Fine Structure (DAFS) spectra have been successfully recorded: soon also this technique will become available for users.

A third experimental hutch at the end of the beamline is available for users who wish to install their own apparatus. An ultra-high vacuum chamber fully equipped for surface preparation and characterization is available for EXAFS investigations in total and partial electron yield mode.

SCIENTIFIC ACTIVITY

The scientific activity of GILDA mainly deals with the study of local structure around atoms present in trace amounts. XAS is a well-suited technique for this: among the experiments performed we recall here the investigations on InAsP/InP and InGaAs/InP superlattices, impurities in semiconductors (Er:Si, Ga:a-Ge, As:Si, Co:Si), impurities (Ag, Cu, Er, Eu, Pr) in various kinds of glasses, metallic active sites in proteins. Catalytic systems have been investigated in cells for *in situ* treatments. The 1997 ESRF-Highlights booklet reported the GILDA studies performed on the metal insulator phase transition in colossal magnetoresistance manganites as well as epitaxial overlayer of InGaAs/InP.

X-ray scattering experiments on amorphous and polycrystalline samples have been performed in the conventional and anomalous modes to obtain a description of the local and medium range order of the whole material and around a particular component. Experiments carried out in this field provided the local order around Eu and Sr in Eu-doped Sr-

metaphosphate glasses, around the metallic components of FeNiB amorphous alloys and around Zr in Zr-based ceramics. Other kind of experiments performed were anomalous powder diffraction on nanocrystalline metallic clusters dispersed on a pumice substrate, anomalous x-ray reflectivity in InAsP/InP superlattices and DAFS on ZnAl₂O₄ and ZnFe₂O₄ spinels.

LOCAL ATOMIC ORDER AROUND ER IN ER-BASED LUMINESCENT MATERIALS

Er doped crystalline Si, exhibiting optical luminescence at 1.54 μm that corresponds to the absorption minimum of commercial optical fibers, represent a promising material for optoelectronic applications. The luminescence arises only from Er⁺³ ions bound to O atoms (usually present in Si as impurities) and the effect is absent in Er-doped high-purity Si. A new way to obtain a high concentration of Er⁺³ active centers consists in performing a double implantation of Er and O ions on a crystalline Si substrate. The as-implanted material undergoes then several annealing treatments to recrystallize the implanted region. Unexpectedly, the as-implanted material exhibited a barely detectable luminescence, strongly increased by the annealing process. To understand this phenomenon, an investigation of the local atomic order around the Er⁺³ ions

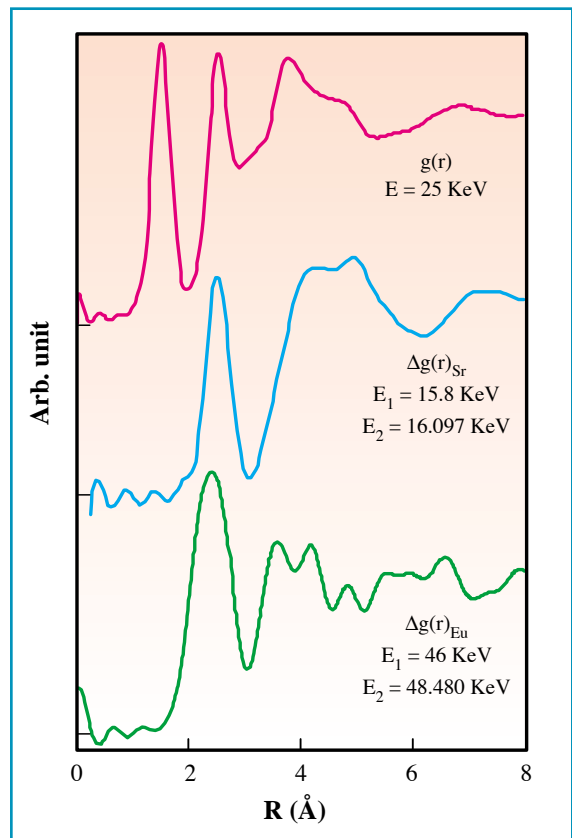


was performed using the Extended X-ray Absorption Fine Structure (EXAFS) technique at the Er L_{III} edge. The typical amount of Er ions in these samples was around 2×10^{15} Er/cm² (roughly 2 ML). In the as-implanted material (process A - Figure 1a) the position of the first FT peak corresponds to an Er-Si coordination with no evidence of Er-O bonds. Er and O do not react, probably due to the extremely reduced diffusion constant of Er in the Si network, and the correspondent luminescence is very low (Figure 1b). The spectra of the annealed samples (B and C) on the other hand show a peak corresponding to an Er-O bond and the luminescent yields are much stronger. Upon annealing, the crystal-amorphous boundary moves towards the surface, creating a region of high atomic mobility where the implanted species can react together and give rise to the active centers.

LOCAL STRUCTURE OF GA-DOPED A-GE:H THIN FILMS

One of the major issues in the physics of amorphous semiconductors is the understanding of microscopic mechanism of substitutional doping in hydrogenated amorphous Si and Ge thin films doped with group III and V elements. In this work hydrogenated

Fig 2: The upper panel reports the Total Correlation Function $g(r)$ for $Eu_{0.1}Sr_{0.9}(PO_3)_{2.1}$ obtained at 25 keV. The middle panel shows the Differential Correlation Function $\Delta g(r)$ obtained at the Sr K edge and in the lower panel is reported the Differential Correlation Function $\Delta g(r)$ obtained at the Eu K edge.



amorphous Ge thin films doped with different Ga concentrations have been investigated by EXAFS spectroscopy. The films were prepared by rf sputtering from a c-Ge target, dopants were added using a co-sputtering technique. The typical thickness of the

films was around 3 μ m, with a Ga amount ranging between 5×10^{14} and 1.3×10^{17} at/cm². Data were collected in fluorescence mode. From the quantitative analysis, the coordination number of Ga at the lower concentration was found to be 4, in

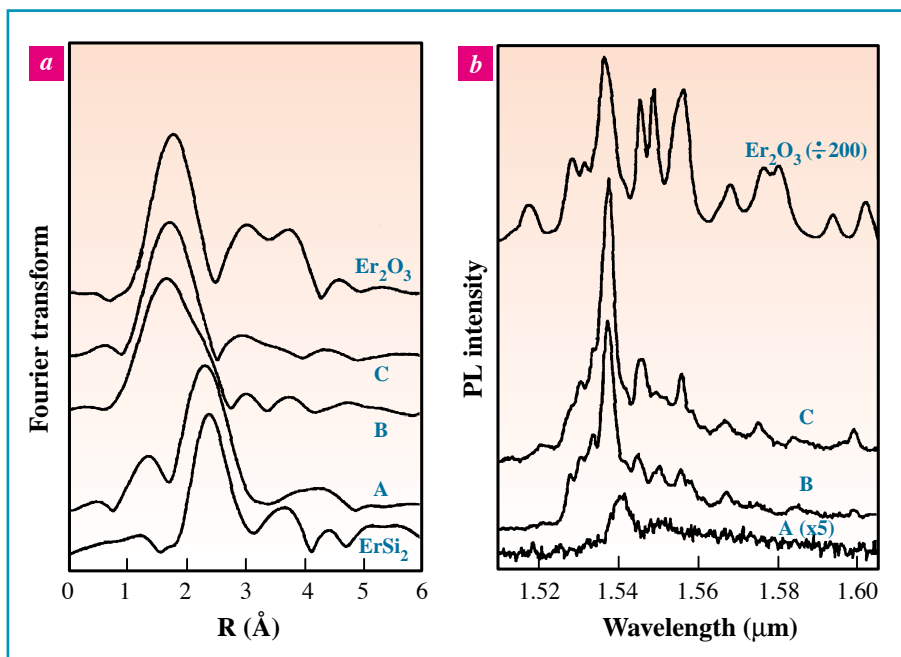


Fig 1: a) Fourier transforms of the EXAFS spectra compared with model compounds for the Er-Si bond ($ErSi_2$ crystal, peak at ~ 2.5 Å) and the Er-O bond (Er_2O_3 crystal peak at ~ 2 Å). b) High resolution photoluminescence spectra at 15 K with a 200 mW laser pump. Capital letters indicate the thermal processes: A = 450°C-30min, B = A+620 °C-180min, C = B+900 °C-30s.



agreement with the hypothesis of substitutional site of the dopant in the Ge tetrahedral network. A sharp decrease in the mean coordination number from 4 to 2.8 occurs when the dopant concentration rises from 4.5×10^{15} to 4.5×10^{16} at/cm² suggesting a Ga site modification at high concentration.

SR AND EU DOPED METAPHOSPHATE GLASSES

Anomalous Wide Angle X-ray Scattering (AWAXS) and extended x-ray absorption fine structure (EXAFS) have been used to investigate the structure of Eu doped Sr metaphosphate glass (Figure 2). In order to investigate both the local structure around Eu and the modifications of metaphosphate network induced by doping two glass samples, a-Sr(PO₃)₂ and a-Eu_{0.1}Sr_{0.9}(PO₃)_{2.1}, were studied at the Sr (16.107 keV) and Eu (48.517 keV) K edges. The resulting model of the host Sr-metaphosphate matrix is consistent with a description of the structure

in terms of Sr²⁺ ions interposed between PO₄ chains. All distances and coordination numbers related to a distribution of PO₄ tetraedra, interconnected via two bridging oxygens, fall within the expected results. However, the location of strontium is more problematic, and the coordination number $N_{\text{Sr-O}} \sim 5$ suggests an irregular distribution of its first coordination shell or an equal number of four-fold and six-fold coordinated Sr atoms. The data obtained on both samples demonstrated that the host metaphosphate matrix is unchanged by doping. The determination of the local structure around Eu by AWAXS at the Eu K edge has been a special issue of this experiment as it is the first attempt to perform an AWAXS experiment at such energies. The choice of one of the three Eu-L edges is also possible to detect the Eu environment, but several problems arise in this case: for the low energy, the reciprocal-space extension of the data is not enough to allow a good resolution of the Eu coordination shells. Moreover, the three L absorption edges are very close each other, making the

measurements more difficult for the lower contrast between the scattering factors of Eu and high fluorescences emission. AWAXS results demonstrated an asymmetric environment around Eu with 7.5 O at 2.32Å and 1.5 at 2.62 Å. ■

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