1 Introduction

GILDA (General Purpose Italian beamLine for Diffraction and Absorption), is the Italian CRG beamline, built to provide the Italian scientific community with an easy access to the European Synchrotron Radiation Facility to perform experiments with a high energy and brilliance X-ray photon beam. GILDA was proposed, designed, constructed and commissioned by a collaboration between LNF and a large number of University groups; it is operative since autumn 1994. Today GILDA is funded by the Italian public research Institutes: Consiglio Nazionale delle Ricerche (CNR) and Istituto Nazionale di Fisica Nucleare (INFN). Experimental stations for X-ray Absorption Spectroscopy, Anomalous X-ray Scattering and X-ray Diffraction (XRD) are present on the GILDA beamline.

The LNF group is involved in the technical maintenance and update of the beamline, with particular emphasis to the electronic and software controls of all the instrumentation and to the apparatus for X-ray diffraction.

2 Summary of the Activity on the GILDA beamline during 2008

During 2008 the main technical works performed on the instrumentation were the test of a Laue diffracting crystal for fluorescence detection, the design, realization and commissioning of the new motorized sample holder for measurements at grazing incidence with high accuracy, a software programme for a complete quantitative data analysis of the ReffEXAFS spectra.

During 2008 about 4000 hours of the 5300 delivered by the ESRF were used for user’s experiments, the remaining for in-house research, beamline improvements, maintenance and alignment. Totally 37 experiments were performed, 25 of Italian users and 12 of European users.

Among the relevant studies performed, we mention the study of the exchange bias effect in Ni/NiO nano-granular alloys; the local structure of Mn-rich nanocolumns; the temperature dependence of the structural parameters of gold nanoparticles and the photoresponse of diamond based solid state ionization chambers.

3 Activity on the GILDA beamline during 2009

During 2009 some implementations on the instrumentation were performed both to increase the reliability of the beamline and its compatibility with the ESRF standard instrumentation. Namely:

1. the vacuum control system of the beamline was upgraded in a new version fully compatible with the ESRF standard one;

2. a new software developed by the ESRF, which control all the items of the front end of the beamline through a single interface, was installed and commissioned;
3. the cooling system of the first mirror was modified to increase the mirror stability;
4. the motor control system in the absorption hutch was upgraded to the ESRF standard icepap based one.

4 Beamtime use during 2009 and scientific outcomes

During 2009 ESRF delivered beam for about 5300 hours; about 4000 hours were used for user’s experiments, the remaining for in-house research, beamline improvements, maintenance and alignment. Totally 34 experiments were performed, 16 of Italian users and 18 of European users.

Studies and results to be mentioned are the followings:

1. The nature of disorder in ordered double perovskite, $\text{Sr}_2\text{FeMoO}_6$ oxides
   The degree of B/B’ alternate cation order is known to heavily influence the magnetic properties of $A_2BB'O_6$ double perovskites although the nature of such disorder has never been critically studied. Our detailed x-ray absorption fine structure studies in conjunction with synchrotron radiation x-ray diffraction experiments on polycrystalline $\text{Sr}_2\text{FeMoO}_6$ samples with various degrees of disorder reveal that a very high degree of short range order is preserved even in samples with highly reduced long range chemical order. Based on these experimental results and with the help of detailed structural simulations, we are able to model the nature of the disorder in this important class of materials and discuss the consequent implications on its physical properties.

2. Proton dynamics in $\text{In:BaZrO}_3$: insights on atomic and electronic structure from X-ray absorption spectroscopy
   The local structure of $\text{Ba}^{2+}, \text{Zr}^{4+}$ and $\text{In}^{3+}$ in $\text{In:BaZrO}_3$ is investigated with EXAFS for samples having 0 to 75% $\text{In}^{3+}$ content. It is found that indium can be inserted in any ratio in the host matrix oxide and that the oxygen coordination shell displays an in-O distance very similar to the Zr-O length. In the Zr-rich compositions, there is a preferred dopant-vacancy association that, however, does not give rise to dopant-proton interaction in the hydrated samples. The tendency of $\text{Ba}^{2+}$ to be attracted toward the dopant site is attributed to the electrostatic interaction with the dopant and to the structural rearrangement around the $\text{In}^{3+}$ site. Third cumulant analysis at high temperatures (up to 673 K) allows to conclude that the anharmonicity of In-O thermal motion is about 1 order of magnitude lower than in other perovskites with higher proton conductivity. It is argued that the lower proton diffusivity displayed by $\text{In:BaZrO}_3$ depends on (a) proton trapping at the dopant site due to the formation of a stable O-H3 3 O hydrogen bond; (b) reduced anharmonicity of the M-O vibrations; (c) different strength of O-H bonds originated by electronic density rearrangement

3. Ag site in Ag-for-Na ion-exchanged borosilicate and germanate glass waveguides
The Ag site in Ag-for-Na ion-exchanged borosilicate and germanate waveguides has been investigated by EXAFS spectroscopy. In contrast with the results generally reported in literature, it is shown that, for both silicate and germanate waveguides, the Ag site is strongly dependent on the Ag content and the Ag-O distance is longer for higher doping levels. It is demonstrated that this trend is related to a structural rearrangement of the Ag site in the whole doped layer; the EXAFS results on the samples that underwent the ion exchange at higher temperatures and the comparison with literature data suggest that the sites with shorter distances are more stable. The correlation between local structure around Ag and the photoluminescence properties of the borosilicate waveguides is established. In particular, the red shift of the blue band observed in the absorption and excitation spectra by increasing the Ag concentration has been univocally related to the increase of the Ag-O bond length.

4. Local structure of (Ga,Fe)N and (Ga,Fe)N:Si investigated by x-ray absorption fine structure spectroscopy


X-ray absorption fine-structure (XAFS) measurements supported by ab initio computations within the density functional theory (DFT) are employed to systematically characterize Fe-doped as well as Fe- and Si-codoped films grown by metalorganic vapor-phase epitaxy. The analysis of extended-XAFS data shows that depending on the growth conditions, Fe atoms either occupy Ga substitutional sites in GaN or precipitate in the form of $\text{Fe}_3\text{N}$ nanocrystals, which are ferromagnetic and metallic according to the DFT results. Precipitation can be hampered by reducing the Fe content, by increasing the growth rate, or by codoping with Si. The near-edge region of the XAFS spectra provides information on the Fe charge state and shows its partial reduction from $\text{Fe}^{+3}$ to $\text{Fe}^{+2}$ upon Si codoping, in agreement with the Fe electronic configurations expected within various implementations of DFT.

5 Beamline Review Panel and future plans

At the end of 2009 the memorandum of understanding between the ESRF and the Italian Institutions INFN and CNR which regulates the beamline activity expired; in view of a renewal of the memorandum in spring 2009 ESRF organized a Review Panel made of internationally well known scientists experts in the field, which reviewed the GILDA scientific activity of the last five years. The Panel judged the activity of excellent quality and suggested ESRF to renew the memorandum and continue the activity for the next five years. This possibility is under consideration of the CNR and INFN.

Moreover since ESRF is doing an extensive refurbishment of the storage ring and of the beamlines, the Panel recommended also a renewal of the beamline instrumentation. At this purpose in December 2009 a two days User Meeting was organized at the University of Palermo for discussing the beamline refurbishment to be implemented during the ESRF shutdown in 2012, to review the scientific activity of the last years and to define a scientific case for the next years. A complete report on the meeting and on the conclusions achieved will be available in the next weeks and will be submitted to the INFN and CNR.
6 2010 - GILDA Foreseen Activity

During the 2010 the activity foresees:

1. the beamline running by approved experiments for at least 4000 hours of user activity;
2. to complete the proposal of beamline refurbishment;
3. to complete the standardization of the beamline motor control

7 Publications

5. F. Giannici et al., Chem. Mat. 21, 2641 (2009).