A comprehensive facility for EXAFS measurements at the INDUS-2 synchrotron source at RRCAT, Indore, India

S Basu, C Nayak, A K Yadav, A Agrawal, A K Poswal, D Bhattacharyya, S N Jha and N K Sahoo
Applied Spectroscopy Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, 400085, India
E-mail: dibyendu@barc.gov.in

Abstract. The EXAFS technique, which deals with fine structure oscillations observed in the X-ray absorption spectrum of an element from 50 eV to ~700 eV above its absorption edge, gives precise information regarding the short range order and local structure around the particular atomic species in the material. With the advent of modern bright synchrotron radiation sources, EXAFS has emerged to be the most powerful local structure determination technique, which can be applied to any type of material viz. amorphous, polycrystalline, polymers, surfaces and solutions etc. Over the last few years a comprehensive facility for carrying out EXAFS measurements with synchrotron radiation over variety of samples has been developed at the 2.5 GeV, Synchrotron Radiation Source (INDUS-2) at RRCAT, Indore, India. The facility consists of two operational beamlines viz., the energy dispersive EXAFS beamline (BL-08) and the Energy Scanning EXAFS beamline (BL-09).

1. Introduction
The Extended X-ray Absorption Fine Structure (EXAFS) technique, with synchrotron radiation as the X-ray source, is a powerful tool to study short range order and local structures around any particular element present in a material. X-ray Absorption Fine Structure (XAFS) is the modulation of an atom’s X-ray absorption probability due to the chemical and physical state of the atom. XAFS spectra are especially sensitive to the formal oxidation state, coordination chemistry, and the distances, coordination number and species of the neighbouring atoms immediately surrounding the probed element. This technique has the added advantage of being element specific and crystallinity of sample is not a prerequisite. X-rays being fairly penetrating in matter, this technique is not inherently surface-sensitive in the transmission mode and average bulk information from a sample can be obtained. XAFS measurements can even be made on trace amounts of elements giving a unique and direct measurement of chemical and physical state of dilute species in a variety of systems by employing data acquisition in fluorescence mode. Surface sensitivity can be imposed by modifying the measurement technique to total electron yield mode. The experimental X-ray absorption spectrum of a sample consists of two regions: X-ray Absorption Near Edge Structure (XANES) (-50 eV to +50 eV around the absorption edge) and Extended X-ray Absorption Fine Structure (EXAFS) (from 50 eV to 700 – 1000 eV above the absorption edge). The former sheds light on the oxidation state of the central atom in a compound whereas the latter gives relevant as information regarding the bond length

1To whom any correspondence should be addressed.
and the coordination number around the probed atom well as disorder factor in the system. The detection of these fine oscillations requires a tunable and bright X-ray source like synchrotron in which radiation is emitted by high energy accelerated electrons. Hence with the advent of modern bright synchrotron radiation sources, this technique has emerged out to be one of the most powerful techniques for local structure determination, which can be applied to any type of material viz. amorphous, polycrystalline, polymers, surfaces and solutions under different ambient and extreme environmental conditions. EXAFS measurement facilities referred to as beamlines, are one of the most significant and extensively used experimental facilities at Synchrotron radiation sources all over the world. 

Over the last few years a comprehensive facility for carrying out EXAFS measurements with synchrotron radiation has been developed at the INDUS-2 Synchrotron Radiation Source at RRCAT, Indore, India. INDUS-2 is a 2.5 GeV 3rd generation machine, presently working at 120 mA beam current (designed for 300 mA) with a horizontal beam emittance of 3.9x10^-9 mrad and a vertical beam emittance of 3.9x10^-9 mrad. The beam stability is good with a noise level of ~2%. The EXAFS facility consists of two operational beamlines built at bending magnet ports of INDUS-2 viz., the Energy Dispersive EXAFS beamline (BL-08) and the Energy Scanning EXAFS beamline (BL-09) [1].

2. Description of EXAFS facilities

2.1 Energy Dispersive EXAFS beamline (BL-08)

EXAFS measurements with synchrotron radiation are generally carried out in two different modes, viz. energy dispersive mode and energy scanning mode. In the dispersive EXAFS mode of measurement, a bent crystal polychromator is used to select a band of energy from the white synchrotron beam horizontally dispersed and focused on the sample. The transmitted beam intensity from the sample is recorded on a position-sensitive CCD detector, recording the whole EXAFS spectrum around an absorption edge in a single shot. This is essentially the working principle of the energy dispersive EXAFS beamline (BL-08) at the INDUS-2 which uses a 460 mm long Si (111) single crystal mounted on a mechanical crystal bender which can bend the crystal to the shape of an elliptical cylinder in such a way that the source and the sample position are at the two foci of an ellipse as evident in figure 1. [2]. The crystal selects a particular band of energy from white synchrotron radiation depending on the grazing angle of incidence of the synchrotron beam (Bragg angle) and disperses as well as focuses the band on the sample.

Figure 1. Optical geometry of BL-08

Figure 2. Optical layout of BL-08

A Rh coated cylindrical pre-mirror with meridional curvature is used for rejection of higher harmonics and vertical focusing of the beam. The radiation transmitted through the sample is detected by a position sensitive CCD detector having 2048 x 2048 pixels. The whole absorption spectrum of the sample can be recorded simultaneously on the detector within fraction of a second. The optical layout of the beamline is depicted in figure 2. The beamline is designed to cover the photon energy range of 5-20 keV providing energy bandwidths of 0.3, 1.0 and 2.0 keV and with resolution of 0.5, 1
and 2 eV per pixel at photon energies of 5, 10 and 20 keV, respectively. The beamline is particularly useful for in-situ and time-resolved studies on samples in transmission geometry.

2.2 Energy Scanning EXAFS beamline (BL-09)

This is the more conventional mode of EXAFS measurement in which the beamline uses a double-crystal monochromator (DCM) to select a particular energy from the incoming synchrotron beam that is incident on the sample. The intensity of the transmitted beam passing through the sample or that of the fluorescence beam emerging out of the sample is recorded along with the incident intensity at each energy. The absorption data of the sample are then recorded by scanning the monochromator over the whole energy range of interest. The Energy Scanning EXAFS beamline (BL-09), which has been commissioned recently, covers a photon energy range of 4-25 keV and has a resolution ($\Delta E/E$) of $10^{-4}$ at 10 keV. The optical layout of the beamline is shown in figure 3.

![Figure 3. Optical Layout of BL-09](image)

A post mirror with meridional curvature is used upside-down for bending the beam path to horizontal.

### Table 1. Beamline Specifications

|                      | BL-08                  | BL-09                  |
|----------------------|------------------------|------------------------|
| **Energy range**     | 5-20 keV               | 4-25 keV               |
| **Energy Resolution (E/$\Delta E$)** | $10^4 @ 10$keV         | $10^4 @ 10$keV         |
| **Flux@ Focus**      | $10^{12}$ photons/sec/1000 eV @ 2.5 GeV, 300mA | $10^{11}$ ph/sec/0.1% bandwidth @ 2.5 GeV, 300mA |
| **Focal spot size**  | 0.20 mm x 0.40 mm      | 0.50 mm x 0.50 mm      |
direction again as well as for vertical focusing of the beam at the sample position. For measurements in the transmission mode, the sample is placed between two ionization chamber detectors. The first ionization chamber measures the incident flux \( I_0 \) and the second ionization chamber measures the transmitted intensity \( I_t \). A third ionization chamber is also used at the end for measuring spectra of reference foils to carry out corrections in energy calibration of the monochromator. It is also possible to carry out measurements in fluorescence mode and a Lytle-type ionization chamber based detector or a Si drift solid state detector is used for this purpose which is placed in front of the sample in a 45° geometry. This beamline is useful for measurement on trace elements, surface studies and thin film materials on a thick substrate.

2.3 Sample environments

In the above two beamlines experiments can be performed in different sample environments. These include a low temperature He-gas cooled closed cycle cryostat which can go down to 4.2 K and a high temperature cell that can go up to 1000K. In the high temperature cell it is possible to carry out measurements under various gaseous environments viz. Cl, H2S, inert gases etc. The sample can also be handled in different forms such as powdered solid compressed to pellet form and sample on tape. A special quartz cell fitted with Be window is also available for measurement of liquid samples. An ellipsoidal mirror for focussing of the beam to <100\( \mu \)m at the sample position is presently being installed at BL-08 to enable measurements under high pressure employing diamond anvil cells. X-ray Magnetic Circular Dichroism (XMCD), for high Z elements utilizing the polarizing property of the synchrotron radiation, and measurements on radioactive samples inside a specially fabricated glove box are planned for beamline upgrades that will augment future programs.

3. Conclusion

An EXAFS measurement facility consisting of two beamlines working in energy dispersive mode and energy scanning mode has been developed and commissioned respectively at BL-08 and BL-09 bending magnet ports of INDUS-2 Synchrotron source at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. The energy dispersive EXAFS beamline is suitable for time resolved studies in transmission mode while in the energy scanning beamline measurement is possible both in transmission and fluorescence mode. Thus these two beamlines are complementary to each other and together they offer a comprehensive EXAFS measurement facility that cover a wide range of samples including dilute materials, thin films, chemical catalysts, liquid etc. This indigenously developed facility is regularly used by researchers from different national laboratories and universities of India and has resulted in a number of research papers in peer reviewed journals. Some of the measurements carried out include studies of Gd, Nd and La doped ZrO2 systems which have potential uses as electrolyte materials for solid oxide fuel cells [3,4]; studies of Eu doped SrSnO3 nanoparticles [5] and Eu\(^{3+}\) doped GaOOH nanorods for their luminescence properties [6]; studies of Sb doped Bi\(_2\)UO\(_6\) which is a potential by-product in high temperature nuclear reactors [7]; and studies of Fe doped CaMnO\(_3\) used as a magnetic material [8].

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