Development, Installation and Commissioning of EDXRD & EXAFS Beamlines at Indus-2 Synchrotron Source

Part-I
Energy Dispersive X-ray Diffraction Beamline at Indus-2 Synchrotron Source

High Pressure & Synchrotron Radiation Physics Division

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Structure of materials is a vital input for determining their physical properties. X-ray diffraction is the most widely used technique, for investigation of structure of materials under various thermodynamic conditions viz., temperature and pressure. There are two variants of the x-ray diffraction technique: Angle Dispersive X-Ray Diffraction (ADXRD) and Energy Dispersive X-Ray Diffraction (EDXRD). EDXRD is known to be an efficient methodology for use in the constrained geometries. In this technique, white x-ray beam is incident on the sample and the diffracted signal is recorded at a fixed angle and is energy analyzed. Since all the reflections are recorded simultaneously, EDXRD is also useful in kinetics related measurements and in glassy systems, where one requires data up to large Q values.

The High Pressure & Synchrotron Radiation Physics Division has developed an EDXRD beamline at a bending magnet port BL-11 of Indus-2 synchrotron radiation source. This beamline has also been optimized for carrying out diffraction measurements at high pressures. The schematic layout of the beamline is shown in Fig 1. Synchrotron Radiation (SR) from abending magnet is transported to

![Schematic of EDXRD beamline](image_url)
the optical hutch of the beamline through the frontend with 1 mrad horizontal beam acceptance. The storage ring vacuum is isolated from the beamline vacuum, by 200 μm thick water cooled beryllium window. The white beam is coarsely defined to ~200 x 200 μm², using a water-cooled primary slit system and as it propagates further, it is collimated to less than 100 x 100 μm², using a set of two precision tungsten slit systems. The sample is mounted on a 8-axis motorized goniometric stage. The goniometer consists of co-axial θ-2θ stage with detector arm, XY translation stage for 2θ axis alignment with SR beam and XYZ stages for sample maneuverability. The diffraction angle and gauge volume of sample is defined, using a set of cleaning slit system mounted on 2θ arm of sample stage. Finally diffraction signal is analyzed using liquid nitrogen cooled energy-sensitive high-purity germanium (HPGe) detector, mounted on the same 2θ arm (Fig. 2). The final resolution of diffraction data at EDXRD beamline is ~2%, limited by the detector resolution. For better inter-planar distance (d_{hk}) resolution and structural determination, one needs to have diffraction data up to higher Q values. In the case of EDXRD beamline, it is determined by the spectral range of white SR beam and the collection angle i.e., 2θ. This beamline provides flexibility of changing the 2θ angle in a range of ±25°, which allows one to record EDXRD pattern up to ~15 Å⁻¹ with energy range up to 70 KeV.

For high pressure experiments, pressure inside Diamond Anvil Cell (DAC) may be monitored, using equation of state of internal pressure calibrant e.g. Au, Cu etc. Since x-ray diffraction peaks from internal calibrants may interfere with the sample diffraction peaks, ruby fluorescence method is widely used. For this, a grain of Ruby is loaded along with the powdered sample inside a DAC. Ruby fluorescence spectrometer installed by us at the beamline, uses 532 nm frequency doubled diode pumped solid state laser as an excitation source and the fluorescence signal is collected using a microscope objective and is analyzed using a spectrograph.

Since this beamline is primarily optimized for high pressure measurements using DAC, where the sample size is ~ 100 μm, a provision has been made to focus white SR beam using Kirkpatrick Baez mirror system. It will focus 200 μm white SR beam to less than ~30 μm with an intensity gain of ~ two orders of magnitude.

First set of benchmark EDXRD patterns of several elemental metals viz. Au, Cu, W, Ta, Zr, Mo etc, were recorded in May, 2008. The energy resolution of diffraction patterns was analyzed and the results are presented in Table 1.

Table 1: Energy resolutions of various diffraction and x-ray fluorescence peaks

<table>
<thead>
<tr>
<th>Peak details</th>
<th>ΔE/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au Lα, (9.713 keV)</td>
<td>0.021</td>
</tr>
<tr>
<td>Au Lβ₁ (11.442 keV), Au Lβ₂ (11.584 keV)</td>
<td>0.026</td>
</tr>
<tr>
<td>Au (111)</td>
<td>0.014</td>
</tr>
<tr>
<td>Au (200)</td>
<td>0.013</td>
</tr>
<tr>
<td>Au (220)</td>
<td>0.012</td>
</tr>
<tr>
<td>Au (311)</td>
<td>0.011</td>
</tr>
</tbody>
</table>
Since then, this beamline is being extensively used for carrying out high pressure EDXRD experiments. A few recent studies using this beamline are discussed below:

**Equation Of State (EOS) measurement of natural Uranium**

At ambient conditions, natural uranium crystallizes in the orthorhombic structure ($\alpha$-U). Previous high pressure experimental and theoretical studies on natural uranium, have shown discrepancy in the compressibility behavior. We have performed high pressure EDXRD experiments on natural U up to 25 GPa. Our measurements show, that ambient $\alpha$ phase is stable up to the highest pressure studied and the bulk modulus and its derivatives are determined to be $B_0 = 108$ GPa and $B_0' = 6.2$ respectively, which agree excellently with the published results obtained at ESRF ($B_0 = 104$ GPa and $B_0' = 6.2$)

**EOS measurement of U- Mo alloy**

Alloys of Uranium, stabilized in body-centered cubic structure ($\gamma$-phase), have been perceived to be more suitable fissile materials. Particularly, U-Mo alloys are formed in the $\gamma$-phase, at a relatively higher range of solute concentration and has an additional advantage of lower parasitic capture cross-section for neutrons. Besides irradiations effects, structural stability as a function of pressure is also important for these materials. We have studied high pressure behavior of U-10 wt. % Mo alloy, stabilized in $\gamma$-phase, up to 63 GPa at our EDXRD beamline. It has been found, that this structure remains stable up to the highest pressure of our measurements.

**High pressure behavior of sesquioxides (Dy$_2$O$_3$, Gd$_2$O$_3$, Yb$_2$O$_3$, Nd$_2$O$_3$)**

Rare earth sesquioxides crystallize in three different structural forms, depending on the rare earth element ionic radius viz. cubic, monoclinic and hexagonal. Larger ionic radii sesquioxides stabilize in hexagonal phase, whereas for smaller ones, cubic phase is more stable. High pressure studies on the cubic and hexagonal structured sesquioxide, would provide further insight into the high pressure structural behaviour of rare earth sesquioxides. Therefore, we carried out high pressure experiments on cubic Dy$_2$O$_3$, Gd$_2$O$_3$, Yb$_2$O$_3$ and hexagonal Nd$_2$O$_3$. Our measurements at the EDXRD beamline showed structural transitions in all these sesquioxides. In particular, cubic phase was shown to transform into hexagonal phase, through a monoclinic phase which is similar to the ambient monoclinic phase found in some sesquioxides. The hexagonal phase of Nd$_2$O$_3$ also showed phase transition to a monoclinic phase at ~27 GPa, but this phase was different from the monoclinic phase, found in case of the other cubic rare earth sesquioxides.

**GIXRD measurements on thin films**

As an extension to the experimental capabilities of our beamline, we have augmented EDXRD beamline for Grazing Incidence X-Ray Diffraction (GIXRD) measurements, in energy dispersive mode. Recently, we carried out GIXRD measurements on various thin film samples viz. LB films of Cd-arachidate of different thickness ranging from 300nm to 1200nm, Co thin film deposited on anisotropically profiled silicon substrate, thin films of Co-Cu, semiconductor TiO$_2$, NbC-Si thin films etc. These experiments were carried out, in order to study the in-plane structure and the effect of SR beam on the thin films, especially in the case of LB films. It has been found, that SR beam degrades LB films depending on the grazing incidence angle of SR beam. Since GIXRD data acquisition is relatively faster and has better signal-to-noise ratio in this mode as compared to that in scanning angle dispersive method, we could study the time dependence of degradation quantitatively, as a function of SR beam exposure.

**References**

Extended X-ray Absorption Fine Structure (EXAFS) technique, enables the measurement of fine structures in the X-ray absorption spectra, above the absorption edge of the atoms in a material. Generally, an EXAFS spectra extends from ~100 eV below the absorption edge of the particular atom to ~700 eV above the absorption edge. The spectrum near the absorption edge (viz., the XANES part) gives information about the long range order existing in the material and the oxidation states of the atoms involved, while the part of the spectrum well above the absorption edge (the EXAFS part) gives information regarding the short range order and local structure around the atomic species. With the advent of modern bright Synchrotron radiation sources, this technique has emerged to be the most powerful, for local structure determination which can be applied to any form or derivative of the material viz. amorphous, crystalline, polycrystalline, polymers, surfaces and solutions.

EXAFS measurements with synchrotron radiation are usually carried out in two different modes viz., scanning and dispersive, targeting different types of sample structures. Under the X plan, the Applied Spectroscopy Division, BARC developed an EXAFS beamline at INDUS-2 Synchrotron source, which works in the dispersive mode, using a 460 mm long Si (111) crystal mounted on an elliptical bender and a position sensitive CCD detector having 2048 x 2048 pixels. The beamline is designed to cover the photon energy range of 5 to 20 keV, providing energy band widths of 0.3 keV, 1.0 keV and 2.0 keV and with resolution of ~ 0.5 eV, 1 eV and 2 eV per pixels, at photon energies of 5 keV, 10 keV and 20 keV, respectively. An optical layout of the beamline is shown in Fig. 1 while the photograph of the beamline is shown in Fig. 2. The emission from the synchrotron source is first passed through a Be window (B) and the beam aperture system (K,K) and is then made to fall on the slit system (S,S).
which defines the final horizontal and vertical divergence of the synchrotron beam, using two sets of water-cooled tantalum jaws. The beam emerging from the slit system falls on vertically focusing mirror (M,M) and then on the silicon crystal (C,C) mounted on a bender. Depending upon the angle of incidence of the beam and its radius of curvature, the crystal reflects a particular central energy ($E_0$) with a certain band-width ($\Delta E$) and this spatially dispersed polychromatic radiation is focused at the sample position (S), which is detected finally by a position-sensitive detector (D,D). Thus, the energy dispersed absorption spectra of the sample, over the whole band width ($E$), can be simultaneously recorded by the detector.

The beamline was commissioned in February 2008. Since then, the beamline has been used extensively and several EXAFS investigations on technologically important materials prepared at various laboratories have been carried out [2,3], as discussed in the following sections:

(i) EXAFS study of uranyl ions, sorbed onto the surfaces of silica and alumina from aqueous suspensions of uranyl nitrate at varying pH have been carried out, at the uranium L_III edge (17.17 keV). The EXAFS analysis shows two oxygen atoms at 1.76 Å (due to axial O=U=O) and varying number of equatorial oxygen atoms (with pH), which were found to be in two groups, corresponding to U-O bond distances of 2.3 and 2.4 Å. These are attributed to the oxygen atoms from coordinated water molecules and those belonging to the silica or alumina surfaces. The above studies are important in modeling the sorption-based immobilization process of high level radioactive waste in silica and alumina rich minerals.

(ii) EXAFS study of binuclear hydroxo-bridged copper (II) complexes have been carried out at Cu K edge on four types of bi-nuclear copper complexes, which are important for their catalytic activity for oxidative coupling reactions[4,5].

(iii) EXAFS measurements have been carried out on doped ZrO$_2$ systems synthesized for Solid Oxide Fuel Cell (SOFC) applications, with 11% Nd and La doping and with 7,9,11 and 13% Gd doping. It has been observed, that though for Gd doping, the oxygen vacancies in ZrO$_2$ host matrix are created near the Zr sites, for Nd and La doping with relatively larger ionic radii, the Zr-O shell remains more or less unperturbed and the oxygen vacancies are located near the dopant cations. It has also been found, that Gd doping of 9% is optimum for creation of vacancies near the Zr sites and hence, for increasing its ionic conductivity.

(iv) EXAFS measurements have been performed on doped BaCe$_{0.8-x}$Zr$_x$Y$_{0.2}$O$_{3-\delta}$ (0 x 0.8) compounds, important for their potential application as electrolytes in SOFC, at the Yttrium K-edge. EXAFS data analysis show BaCe$_{0.8-x}$Zr$_x$Y$_{0.2}$O$_{3-\delta}$ compounds to have the orthorhombic structure for x = 0.6 and tetragonal structure for x = 0.8, which is consistent with X-ray diffraction measurements.

(v) EXAFS measurements have been carried out on two types of magnetically important ferrite spinel systems (a) magnetite doped with 50 mol % of Co and Zn (Co$_{50}$Zn$_{50}$Fe$_{2}$O$_{4}$), and (b) magnetite doped with 50 mol% Co and Ni (Co$_{50}$Ni$_{50}$Fe$_{2}$O$_{4}$). Analysis of EXAFS spectra has shown, that the bond distances of all samples are slightly higher than that expected for pure magnetite (Fe$_{3}$O$_{4}$) sample, due to the presence of the larger size dopant cations (Co, Ni and Zn) in the Fe sites.

(vi) EXAFS measurements have been carried out on ZnO nanoparticle gas sensors with varying particle size (between 5-100 nm) at the Zn K-edge (9659 eV). It was observed that for all the samples, the first Zn-O shell has lower coordination than the nominal value, which is a manifestation of presence of oxygen vacancies in the ZnO samples as expected. It was also observed, that with decrease in the particle size of the ZnO samples, Zn-Zn site is mostly affected with a gradual decrease in coordination number and increase in the Debye-Waller factor and bond distance.
Presently, *in situ* measurements in the beamline up to 600 K under different ambients is possible and facilities to carry out experiments in low temperatures up to 10 K and high temperature up to 1200 K, will be introduced soon.

**Acknowledgements**

The front-ends of both the beamlines were installed by our colleagues from the Synchrotron Utilization Division of RRCAT, Indore. Developments of several components of the beamlines, such as primary slit, precision slits and installation of goniometer of EDXRD beamline and crystal-bender and 19-axes goniometer for EXAFS beamline were done with the help of several colleagues of CDM (group leader Sh. A.K. Sinha) who were also the co-recipients of the group achievement award.

**References**