



Chapter 2

Experimental:

Procedure

and

Characterization

Techniques

2.1 Sample Synthesis

2.1.1 Solid State Reaction Technique

The **solid-state reaction route** is the most widely used method for the preparation of polycrystalline solids from a mixture of solid starting materials. Solids do not react together at room temperature over normal time scales and it is necessary to heat them to much higher temperatures, often to 1000 to 1500 °C in order for the reaction to occur at an appreciable rate. The factors on which the feasibility and rate of a solid state reaction include, reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity and the thermodynamic free energy change associated with the reaction.

In solid state reaction technique, reactant chemicals were taken in required stoichiometric ratio and mixed thoroughly. After mixing, the solid mixture was heat treated at higher temperature for several hours with intermediate grindings. Prior to heat treatment, pelletization of samples are preferred since it increases the area of contact between the grains. Detailed process has been given in working chapters.

2.2 Experimental Techniques & Their Working Principle

2.2.1 X-ray Diffraction

X-Ray diffraction is a technic mostly used to study the crystal structure of material or confirm the single phase of sample. It mean XRD is the “finger print” of the material because it identify the structure of compound belong to what family of crystal structure. Diffraction can occur when any electromagnetic radiation interacts with a periodic structure. The repeat distance of the periodic structure must be about the same wavelength of the radiation. X-rays have wavelengths on the order of a few angstroms (In our case 1.5418 Å). This is the typical inter-atomic distance in crystalline solids, making X-rays the correct order of magnitude for diffraction of atoms of crystalline materials. When X-rays are scattered from a crystalline solid they can constructively interfere, producing a diffracted beam.

2.2.2 Neutron Diffraction

Neutron diffraction technique is a powerful tool to study the structural and magnetic properties of materials in condensed matter physics and also in other field of sciences. Neutrons are neutral and deeply penetrating unlike other radiation sources e.g. x-ray and electrons. Its wavelength is the order of inert-atomic distances in solids and

liquids due to elastic scattering gives better information about structure in condensed matter physics. The energy of the neutron is the order of lattice vibrations, magnetic excitations, diffusive motions due to inelastic scattering get the information about dynamics in condensed matter physics. Neutrons particles have spin ($s=1/2$) when it interacts with spin component of material get the magnetic structure. Properties of neutrons are given below.

Mass = 1.674×10^{-27} Kg

Wavelength $\lambda = h/mv = h/ (2mE)^{1/2} = 0.0286/E^{1/2}$ [E is the Kinetic Energy(K.E.)]

Charge = 0

Spin (s) = $1/2$

Magnetic dipole moment $\mu_N = -1.913$

Neutron life time

$\xrightarrow{15 \text{ min}}$ n \longrightarrow p + e + $\bar{\nu}$

Neutron production

Reactor source

$N + U^{235} \longrightarrow {}^{36}\text{Ba} + {}^{56}\text{Kr} + \text{neutron} + \text{betas}$

The fission neutrons have high KE 1-15 MeV

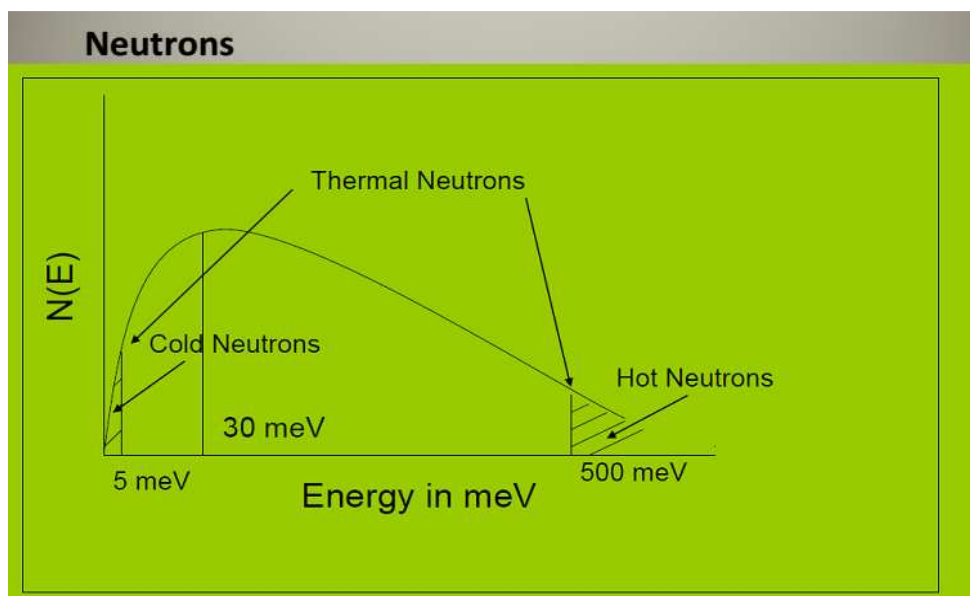


Fig. 2.1: Energy range of neutrons

Schematic diagram of neutron Diffractometer set up PD-2 (Powder Diffractometer-2) at Bhabha Atomic Research center, Mumbai, India given below.

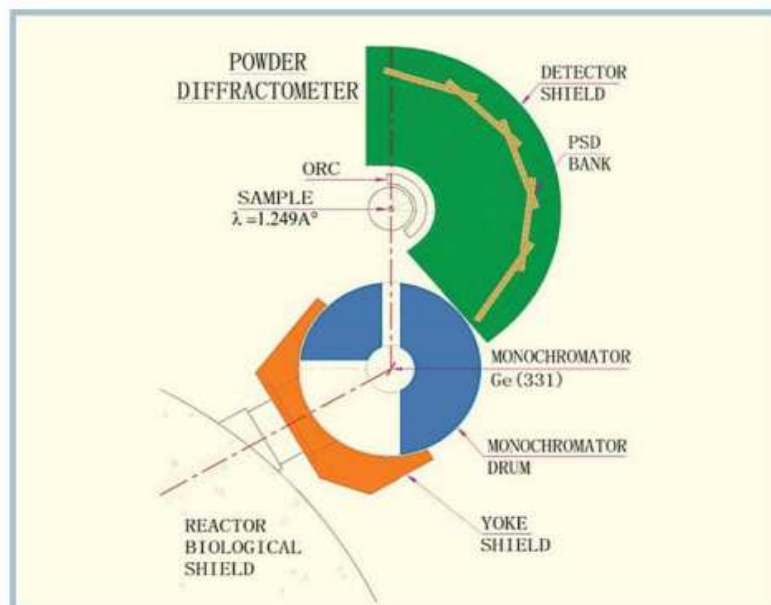


Fig. 2.2: Setup PD-2 (Powder Diffractometer-2) at Bhabha Atomic Research Center, Mumbai, India.

2.2.3 Superconducting Quantum Interference Device (SQUID)-Magnetometer

Superconducting quantum interference device SQUID magnetometry is well-known as one of the most sensitive methods of magnetometry. This technique uses a combination of superconducting materials and Josephson junctions to measure magnetic fields with resolutions up to 10^{-14} T or better.

Principles

A radio frequency (RF) SQUID is made up of one Josephson junction, which is mounted on a superconducting ring. An oscillating current is applied to an external circuit, whose voltage changes as an effect of the interaction between it and the ring. The magnetic flux is then measured.

The DC SQUID A DC SQUID is actually a rather simple device which consists of two Josephson junctions connected in parallel on a closed superconducting loop as shown in Fig. 2.3 (a).¹ A fundamental property of superconducting rings is that they can enclose magnetic flux only in multiples of a universal constant called the flux quantum, $h/2e = 2.07 \times 10^{-15}$ Wb. Actually the flux quantum is very small due to which this physical effect can be exploited to produce an extraordinarily sensitive magnetic detector known as the SQUID. SQUIDs work as magnetic flux-to-voltage transducers where the

sensitivity is set by the magnetic flux quantum. Applying current to the SQUID (biasing it) sends Cooper pairs of electrons tunneling through the junctions. A magnetic field applied to the ring, however, alters the flow. Specifically, it changes the quantum-mechanical phase difference across each of the two junctions. These phase changes, in turn, affect the critical current of the SQUID. A progressive increase or decrease in the magnetic field causes the critical current to oscillate between a maximum value and a minimum one. The maximum occurs when the flux administered to the SQUID equals an integral number of flux quanta through the ring; the minimum value corresponds to a half-integral number of quanta. The flux applied to the SQUID can assume any value, unlike the flux contained within a closed superconducting ring, which must be an integral number. In practice, we do not measure the current but rather the voltage across the SQUID, which also swings back and forth under a steadily changing magnetic field as shown in Fig. 2.3(b). This quantum interference effect provides us with a digital magnetometer. Each "digit" represents one flux quantum. In fact, conventional electronics can detect voltages corresponding to changes in magnetic flux of much less than one flux quantum. Thus the SQUID in essence is a flux-to-voltage transducer, converting a tiny change of magnetic flux into a voltage.

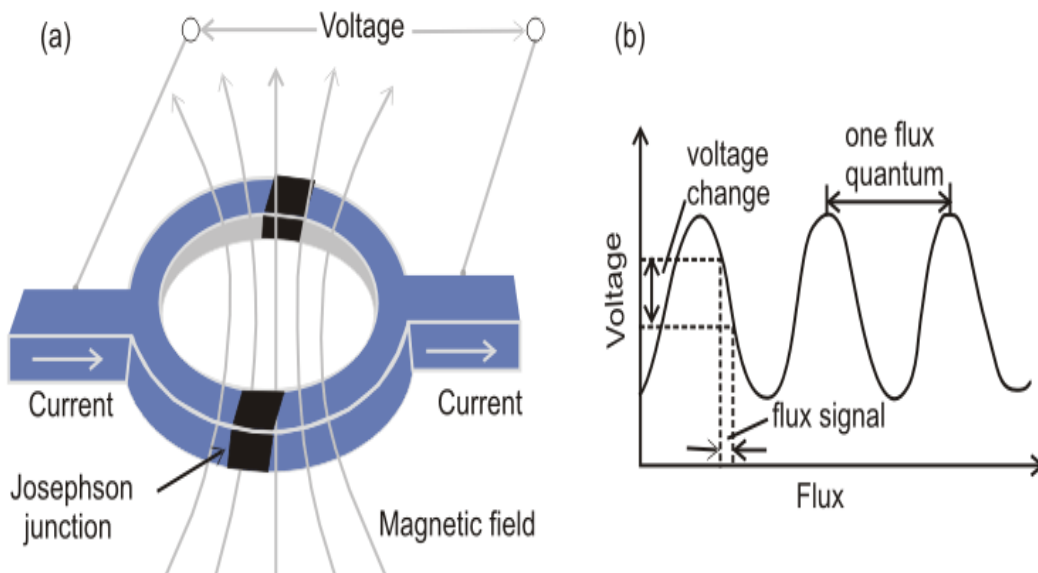


Fig. 2.3: *The DC SQUID construction and principle: (a) Shows the two Josephson junctions forming a superconducting ring.(b) Shows the output voltage as a function of applied flux. A tiny flux signal produces a corresponding voltage swing across the SQUID, which conventional electronics can measure. Figure inspired by Ref. ¹*

2.2.4 X-ray Photoemission Spectroscopy(XPS)

X-Ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a powerful analysis technique used to obtain chemical information about the surfaces of solid materials. Both composition and the chemical state of surface constituents can be determined by XPS analysis.² Insulators and conductors can easily be analyzed in surface areas from a few microns to a few millimeters across. XPS is a surface sensitive technique because only those electrons generated near the surface escape and are detected. The photoelectrons of interest have relatively low kinetic energy. Due to inelastic collisions within the sample's atomic structure, photoelectrons originating more than 20 to 50 Å below the surface cannot escape with sufficient energy to be detected.

Working principle: The sample is placed in an ultrahigh vacuum environment (typically $\sim 10^{-10}$ torr) and exposed to a low-energy, monochromatic x-ray source. The incident x-rays cause the ejection of core-level electrons from sample atoms. The energy of a photoemitted core electron is a function of its binding energy and is characteristic of the element from which it was emitted. Energy analysis of the emitted photoelectrons is the primary data used for XPS. When the core electron is ejected by the incident x-ray, an outer electron fills the core hole. The energy of this transition is balanced by the emission of an Auger electron or a characteristic x-ray. Analysis of Auger electrons can be used in XPS, in addition to emitted photoelectrons.

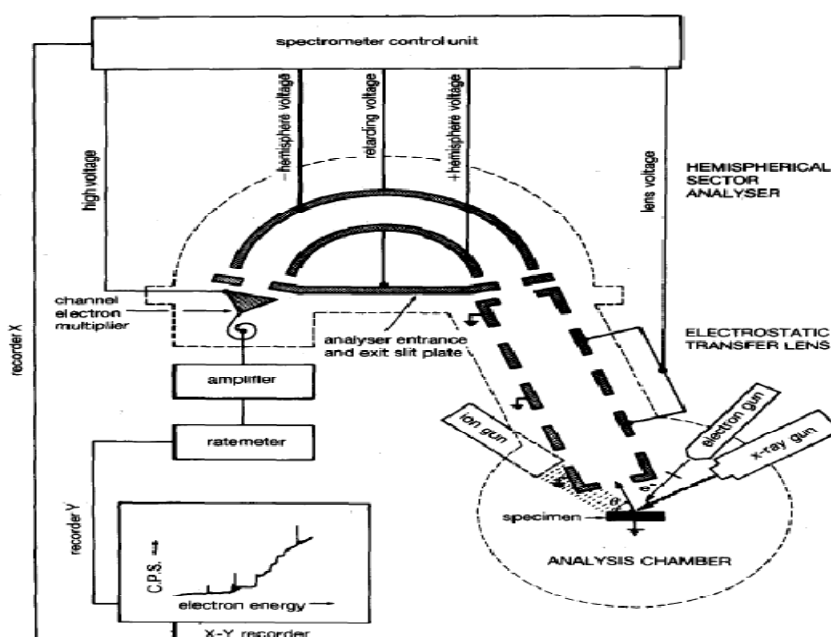


Fig.2.4: Schematic diagram of X-ray photoemission spectroscopy.

The electron binding energy of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):

$$E_{\text{Binding}} = E_{\text{Photon}} - (E_{\text{Kinetic}} + \phi) \quad (2.2)$$

where E_{Binding} is the binding energy (BE) of the electron, E_{Photon} is the energy of the X-ray photons being used, E_{Kinetic} is the kinetic energy of the electron that measured by the instrument and ϕ is the work function of the spectrometer (not the material).

2.2.5 Raman Spectroscopy

Raman spectra, discovered by Raman and Krishnan in 1928³, has been developed as a novel qualitative and quantitative optical technique by the scattering of radiation. Raman spectroscopy is a brilliant spectroscopic technic based on the inelastic scattering of monochromatic light, usually a laser source. Inelastic scattering of light means that the frequency of photon changes when it interacts with a sample. Photons of laser light are absorbed by the sample and then it reemitted. In this way, there is a shift in the frequency of reemitted photon is observed in comparison with original frequency of monochromatic source which is termed as “Raman effect”. This shift in the frequency evolved information about vibrational, rotational and other low frequency transition in molecules.⁴

Selection Rule for Raman Spectra

Raman effect is based on molecular deformation in electric field E determined by molecular polarizability α . The laser beam can be considered as an oscillating electromagnetic wave with electric vector E . After interaction with sample it induces electric dipole moment $P = \alpha E$ which deforms molecule. Due to the periodical deformation, molecules start vibrating with characteristic frequency ν_m . Amplitude of vibration is defined as nuclear displacement or it can be understand by another way, monochromatic laser light ν_0 excites molecules and transforms them into oscillating dipoles. That oscillating dipoles emit light of three different frequencies such as ν_0 , $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$ which are known as Rayleigh, stokes and Anti-stokes scattering (as shown in figure 2.5).

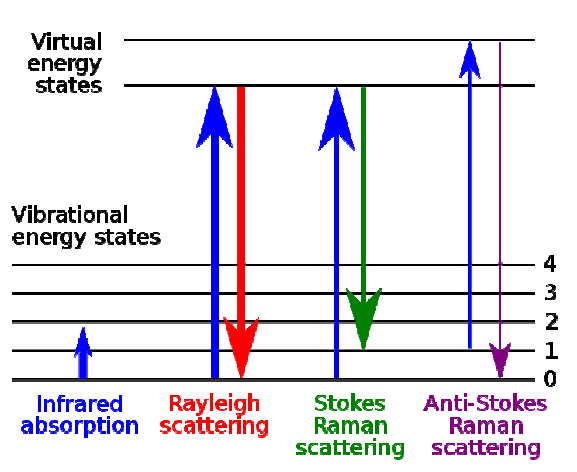


Fig.2.5: Energy level diagram showing states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.

2.2.6 Swift Heavy Ion Beam Irradiation (SHI)

Defect engineering in materials is of importance. The two parameters of ion beam, which play crucial role in defect engineering, one is the ion mass and other its energy, which decide the magnitudes of the electronic as well as nuclear energy losses. The other interesting aspect of Swift Heavy Ions is the characterization of materials by Elastic Recoil Detection Analysis. Production methods for new materials, modification of material properties mainly with the use of Swift Heavy Ions (SHI), and elemental analysis capability are available at the Centre, giving unique opportunities to material scientists.⁵In recent studies, ion beam irradiation technic have been mostly used to study the surface modification and creating some defects to enhanced or modify physical properties like magnetic and dielectric etc. Swift heavy ion beam irradiation is best tool for tailoring material and creating defects in materials in condensed matter physics.

Working principle

A swift heavy ion when passing through material loses its energy either by elastic collisions with nucleus (nuclear stopping power S_n $[-dE/dx]_n$) or by inelastic collisions with electrons (electronic stopping power S_e $[-dE/dx]_e$). In the energy region around 1MeV/amu the nuclear energy loss becomes negligible and electronic loss dominates ($S_e \gg S_n$). It has already confirm that amorphized latent tracks are produced above threshold value of S_e , i.e S_{eth} ($S_e \gg S_{eth}$) corresponding to a large electronic excitations. Amorphized latent tracks strongly modify the magnetic properties of magnetic insulator.⁶

SHI irradiation was performed at Inter University Accelerator Centre (IUAC), New Delhi, India, using a 15 UD tandem accelerator. 150 MeV Ag^{+11} ion beam with a beam current ~ 0.3 pA (particle nano ampere) was used with ion doses of 5×10^{11} ions / cm^2 , 1×10^{12} ions / cm^2 and 5×10^{12} ions / cm^2 . Intensity of ion beam irradiation is defined as the exposer time of ion beam incident on the sample i.e. to increase the intensity of irradiation increases exposer time means increase the bombardment of high energy ion as calculated by a formulae based on exposer time.

References

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