# CHAPTER 4

## EXPERIMENTAL TECHNIQUES

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4.1 Introduction

A proper understanding of the experimental technique and the instruments used is necessary before subjecting them to fruitful research. In the present work, a number of experimental techniques, such as optical microscopy, electron microscopy, X-ray diffraction, conductivity measurements, dielectric measurements using microwaves, microhardness measurements etc. have been employed. A brief account of the materials and methods is given as under.

4.2 Silvering Technique

The crystal surfaces and the optical flats
have to be coated with a highly reflecting layer of silver for microscopic studies. The principle of this method is to thermally evaporate silver on to the specimen at low pressure. A commercial vacuum coating unit (fig. 4.1) "Edwards 12 EA" (England) was used for this purpose. The vacuum chamber was evacuated by a three stage silicon oil diffusion pump backed by an oil rotatory pump. The vacuum at different stages was measured by pirani gauge and Philips ionisation gauge built in the unit. The surfaces were thoroughly cleaned before the deposition of silver. The cleaning process of surfaces depended very much on the nature of surfaces. Optical flats were first cleaned with nitric acid, washed with water after applying soap and then with hydrogen peroxide. Thereafter, they were cleaned by rubbing with dry cotton wool till no breath figure was formed on breathing over them. Freshly cleaved crystal surfaces did not require any cleaning. Final cleaning was done by ionic bombardment in the vacuum coating unit by means of a high tension discharge.

When the pressure was about $1 \times 10^{-5}$ torr spectroscopically pure silver was evaporated from a molybdeum boat by passing a low tension high current. In order to protect the surfaces to be coated from receiving the vapours of burnt impurities, while heating
the boat it was covered with an adjustable shutter. Silver was deposited for the required time by removing the shutter from above the boat.

4.3 Microscopes Used

4.3.1 Incident light microscope 'Epignost'

Preliminary optical microscopic examination of the crystal surfaces as well as photographic recordings at relatively lower magnifications are performed using Carl Zeiss Jena (West Germany) 'Epignost' incident light microscope. This microscope can be conveniently used for rapid examination of surfaces of crystals. Being an incident light type of microscope, the objective has an infinite intersectional distance i.e. the specimen lies in the front focal plane of the objective and its image is formed at infinity. The instrument contains a permanently built in tube lens which together with the eye piece forms a telescope, thus resulting in a factor of 0.63 for calculating the total magnification. Magnification from 11 to 197 could be attained in certain steps in this microscope. A 6V, 15W filament lamp serves as the source of light.

The epignost with a photomicrographic 'MF' equipment in combination with a miniature 35 mm camera
(fig. 4.2) can be excellently used for the photomicroscopic work.

4.3.2 Vickers' projection microscope

Vickers' projection microscope (England) has been used for microtopographical studies, and is shown in fig. 4.3. This is an inverted type of metallurgical microscope in which the specimen to be studied is placed in a movable stage above the objective lens. The flexible illuminating system which can be used both for transmission and reflection photography consists of a powerful mercury lamp, pointolite or carbon arc lamp, a condenser and an aperture controlled iris diaphragm. For visual observations, an eye piece with a reflector is pushed into the tube below the objective. This completes the normal microscope system. For photomicrography, a projection eye piece is used and the final image is focussed on the projection screen after reflection from the projection mirror. A slight refocussing is, of course, necessary when the visual system is changed to the projection system. A total magnification X 25 to X 4550 can be attained in certain steps with this microscope.

4.4 Indentation Technique

In order to study the microhardness of
the crystals the indentation technique is employed. The necessary equipment for the purpose is always to be attached to the Vickers' projection microscope, and is shown in fig. 4.4. The various components as numbered in the figure are as follows:

1. Filar micrometer eye piece in centering mount.
2. Tube length scale for magnification setting.
3. Base plate contact anvil.
4. Beam contact tip.
5. Collect chuck securing specimen.
6. Chemical balance weights to apply load.
7. Load centre indicator.
8. Red signal lamp.
9. Auxiliary counter weight.
10. Counter weight.
11. Diamond indentor objective
12. Power supply for signal lamp.

The specimen to be indented is mounted on a circular aluminium disc and inserted in the collect. The beam is then balanced by the addition or removal of counter weights in such a way that the contact was just made which can be indicated by flickering of the red signal lamp. A required load is then applied. The region to be indented is scanned with the help of the reading
objective and then the diamond indentor is properly placed. After lowering the stage to bring the indentor near the crystal test surface, the diamond indentor is raised with the help of fine motion mechanism until it just makes a contact with the test surface. Then it is lifted sufficiently to break the electrical contact. The contact is normally maintained for, say, 30 seconds. By reversing the motion, the indentor is removed and the indented region examined with the reading objective through the filar eye piece.

The diagonals of such indentation marks are measured and Vickers' Hardness Numeral (VHN) is calculated using the formula

$$VHN = \frac{2p \sin \theta/2}{d^2} \text{ kg mm}^{-2}$$

where $p$ is the load applied on the indentor in units of kilogram weight, $\theta$ is the angle between the opposite faces of the indentor and $d$ is the average diagonal length in mm.

For $\theta = 136^\circ$, as is the case with the Vickers pyramidal indentor, the formula simplifies to

$$VHN = \frac{1.854 \times p}{d^2} \text{ kg mm}^{-2}$$
4.5 X-ray Diffraction Technique

The X-ray analysis has been carried out using the Philips X-ray generator type PW 1009 (Holland) shown in fig. 4.5. This X-ray unit provides continuously adjustable high voltage, 0-55 kV and tube current 0-40 mA.

In a powder diffractometer, the diffracted radiation is detected by counter tubes which move through angular range of reflections. The intensities are recorded on synchronously advancing strip chart. The powder diffractometer, shown in fig. 4.6, consists of the X-ray generator TUR M61 made by VEB Transformatoren und Rontgen werk Dresden, the horizontal counter goniometer HZG 3 and the linear momentum density recorder VAD 53-1 made by Freiberger Prazisions Mechanik GDR. A selection of five different goniometer angular velocities of $1/12^\circ\text{min}^{-1}$ to $2^\circ\text{min}^{-1}$ and various recorder chart speeds are available. Determinations with the diffractometer, in general, require approximately 100 times more of the substance than the conventional Debye-Scherrer methods. Compared with the photographic methods, the diffractometry, in most cases, offers essential advantages due to the higher sensitivity, the higher resolving power, the accuracy of the intensity measurements and the elimination of the elaborate work in dark room. Above all, the diffractometric records can
be obtained in a much shorter time than with photographic method.

For obtaining rotation and/or Weissenberg photographs, the crystal is carefully mounted and bathed in the X-ray beam while being rotated through 360° about its axis, or oscillation through a smaller angle. The camera used for taking rotation and Weissenberg photographs, is shown in fig. 4.7.

4.6 Electron Microscope

In the present investigation electron microscope stereoscan S-4-10 was used for two purposes: (1) microprobe analysis and (2) scanning the surfaces of the grown crystals.

4.6.1 **Electron microprobe analysis**

Electron microprobe analysis has been increasingly used, particularly to study variations in the concentration of an element in the region near the surface of a crystal. It is probably the most powerful method for investigation of compositional gradients. A strong beam of electrons is injected on the crystal surface. As a result each excited element in the crystal emits X-rays of its characteristics wavelengths. A
spatial resolution of less than 1 \( \mu m \) is possible with electron microprobe analyser. A schematic diagram of an electron microprobe analyser is shown in fig. 4.8. The idea of this technique was first patented by Hilliar[^2] but the first instrument was constructed by Castaing[^3]. The specimen is mounted on a stage which can be displaced or rotated, and is observed through a microscope so that it can be continuously viewed in order to select a particular region for analysis. An area of the specimen is usually scanned and an image is simultaneously observed at a number of wavelengths corresponding to the constituent elements. The instrument is combined with a scanning electron microscope.

The electron beam causes local heating of the sample. Hence sample must be stable in vacuum at high temperatures. This problem is encountered only with insulating samples. This can be overcome by coating the surface with a thin layer of carbon. This layer also serves to prevent charging of the sample and so stabilizes the electron beam.

4.6.2 **Scanning electron microscope**

The scanning electron microscope has resolution of about 100 \( \mu m \). In the normal mode of operation,
electrons accelerated by a potential 5-50 kV are directed on the sample, and the scanning coils cause the beam to move across the specimen in a square raster. The secondary electrons which are emitted from the specimen strike the collector electrode and the resulting current is amplified and used to modulate the brightness of a corresponding spot which is displayed on a cathode ray tube. The time associated with emission and collection of secondary electrons is negligible compared with the time of the scan, and so the number of secondary electrons collected from any point on the specimen is determined only by the "brightness" of the spot. Image contrast can arise from a number of factors, particularly surface topography, atomic number, electrical conductivity, specimen orientation and electric or magnetic fields.

4.7 Electrical Conductivity Measurement

The Million Megohmeter, Model 2M 160 MK III A manufactured by BPL India, has been used for the electrical conductivity measurements. The ranges of measurements possible with this meter is from 10 million ohm to 400 tera ohm and current down to 1.0 pico ampere. This self contained instrument is provided with DC test voltages of 10 V, 50 V, 100 V, 250 V, 400 V, 500 V and 1000 V.
An automatic, built-in delay circuit computes the charging delay time required for the test sample. Since the delay calculator indicates an over load protection, the lamp will also flash if the test sample breaks during test, or should the range selected is too sensitive.

4.8 Dielectric Measurement with Microwaves

At microwave frequencies the dielectric properties of material can be obtained accurately only by measuring the wavelength in the material or its reflecting power and attenuation of the wave in the material. The method of measurement of dielectric properties of solid dielectrics described by Roberts and Von Hippel has been developed by Dakin and Works. This method consists of reflecting the wave at normal incidence from a slab of dielectric which is placed at a short circuited end of a wave guide. The process of reflection sets up standing waves in the wave guide in front of the sample as a result of the superposition of the incident and reflected waves. The separation of first minimum from the face of the sample will depend on wavelength of the wave in sample and its thickness. Insertion of the dielectric shifts the minima of the standing wave towards the end. The separation of the first minimum of
the standing wave from the surface of the sample is a measure of dielectric constant. The process of reflection sets up standing waves in the space region in front of the sample as a result of the superposition of the incident and reflected wave is shown in fig. 4.9.

4.9 Magnetic Susceptibility Measurements

The magnetic permeability ($\mu$) of a compound in a magnetic field is given by the equation,

$$\mu = 1 + 4\pi K$$  \hspace{1cm} (4.1)  

where $K$ is the volume susceptibility of the material. The quantity often calculated is the magnetic susceptibility per gram ($\chi$) which is defined as $\chi = k/d$, where $d$ is the mass density of the material used for study.

Diamagnetism arises from the electrons in closed shells tending to orient their planes of rotation so as to suffer minimum interaction with the imposed magnetic field. All the diamagnetics are characterised by negative values of $k$ and $\chi$. Paramagnetism arises from the angular moments, orbital and/or spin associated with the unpaired electrons. For all paramagnetic substances $k$ and $\chi$ are positive.
Ferromagnetism and antiferromagnetism are subdivisions of the paramagnetism and are known as "co-operative phenomenon", which means that they arises when the paramagnetic centres within a sample interact magnetically with each other.

In order to detect and determine the magnetic susceptibility of a given test sample, it is first finely powerded and then packed in a glass container whose weight is exactly measured using an sensitive Gouy balance (fig. 4.10) the pan of which is situated between two powerful electromagnets. The increase in weight after applying the magnetic field is measured for the calculation of magnetic susceptibility using the relation,

\[ \chi = \frac{\mathcal{C} + \beta}{w} \frac{dw}{w} \]  \hspace{1cm} (4.2)

where \( \mathcal{C} \) is the correction due to air displacement
\( \beta \) = constant for glass
\( w \) = weight of the sample
\( dw \) = change in weight on applying electric field.
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