Chapter 2

EXPERIMENTAL PRINCIPLES AND INSTRUMENTATION

2 Introduction

A brief description of the various characterization techniques used in the present work has been discussed in this chapter. Single crystal X-ray diffractometer was used for confirming the crystal structure and / or elucidate three dimensional arrangement of atoms in the grown crystals. Spectroscopic methods are widely used for qualitative and quantitative analyses of synthesized chemical compounds. Thermogravimetric analyzer, differential thermal analyzer and differential scanning calorimetry have been used for studying the thermal stability of the crystals. Vickers microhardness test is used for investigating the mechanical strength of the crystals.

2.1 X-ray diffraction analysis

The architecture of molecules can be derived from studies on the diffraction of X-rays by crystals. In 1912 German Physicist Laue [1] suggested that a crystal which consisted of a three dimensional array of regularly spaced atoms could serve the purpose of a grating. This method was first used by Bragg in 1913 [2]. Since then X-rays have helped to establish detailed features of the molecular structure of every kind of stable chemical species in a crystalline form, from the simplest to those with many thousands of atoms.

2.1.1 Powder X-ray diffraction analysis

Bragg showed that scattered radiation from a crystal behaves as if the diffracted beam was reflected from a plane passing through the points of the crystal lattice in a way that makes these crystals - lattice
planes analogous to mirrors. From such considerations Bragg derived the famous equation

\[ n\lambda = 2d_{hkl} \sin \theta \]  

(2.1)

Where \( \lambda \) is the wavelength of the radiation used, \( n \) is an integer (analogous to the order of diffraction from a grating so that \( n\lambda \) is the path difference between waves scattered from adjacent lattice planes with equivalent indices), \( d_{hkl} \) is the perpendicular spacing between the lattice planes in the crystal and \( \theta \) is the complement of the angle of incidence of the X-ray beam. The geometrical relationships are shown in Fig. 2.1.

![Fig 2.1 Diffraction of X-rays from a set of crystal planes](image)

With a powdered crystalline specimen many different orientations of tiny crystallites are present simultaneously. For any set of crystal planes, Bragg's law will be satisfied in some of the crystallites, so the complete diffraction pattern will be observed for any orientation of the specimen with respect to the X-ray beam. Powder X-ray diffraction is an extremely powerful non destructive tool for identifying crystalline phases and qualitatively and quantitatively analyzing mixtures. It is used to analyze unit cell parameters as a function of temperature and pressure and to determine phase diagrams. Compilations of common powder diffraction patterns are maintained by the Joint Committee for Powder Diffraction Standards (JCPDS).
However in powder X-ray diffraction we lose the three dimensional information we can obtain from single crystals. This makes it much harder to solve structures by powder diffraction alone. However sophisticated methods, originally introduced by Rietveld in 1967 [3] give precise unit cell dimensions, atomic coordinates and temperature factors for adjusting parameters with an experimental powder diffraction pattern. This is of course invaluable when suitable large crystals cannot be grown.

We used a powder diffractometer with Bragg geometry using Cu source available at the Nuclear Physics department of University of Madras. In this system, the source, the detector and the sample are oriented in the same direction and occupy three consecutive positions on a circumference. This configuration guarantees the same Bragg conditions for a large area of the sample. The positions of the source and the detector vary in a synchronous way, always maintaining a symmetrical position, while the sample is always fixed. In this way we obtain a discrete pattern of the reflections for the families of planes that are parallel to the surface of the sample when the source and the detector take on different 2θ angles.

2.1.2 Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction is used to determine the basic geometry (the space group and lattice parameters) of individual crystals, their structure and the positions of the atoms in the lattice.

In the rotating crystal method monochromatic X- radiation is incident on a single crystal that is rotated about one of its axes. The reflected beams lie as spots on the surface of cones that are coaxial with the axis. The diffracted beam directions are determined by intersection of the reciprocal lattice points with the sphere of reflection. Analysis of the diffraction angles produces an electron density map of the crystal. It is only necessary to find the atomic arrangement in one unit cell, which can
be derived from the overall intensity variation in the diffraction pattern, and then repeat it according to the direct lattice to give the entire crystal structure. The spatial arrangement of the diffracted beams is determined by the geometry of the crystal lattice and the intensities are determined by the arrangement of atoms within one unit cell.

Data collection (the result of a systematic rotation of the single crystal with respect to the X-ray beam) produces a complete set of data comprising a list of peak positions ($hkl$ indices of the reflections) and the corresponding intensities. A first electron density map is calculated from these results, the mathematical refinement techniques are used to improve the approximate atom coordinates obtained from the imperfectly phased Fourier synthesis. Refinement obtains final coordinates and, for each atomic position, a displacement or thermal parameter. The geometry of the molecule (bond lengths, valence and torsion angles) can be derived from the atomic coordinates. Information about the intramolecular forces that stabilize the various molecules can also be derived by analyzing the crystal packing [3].

We used a CAD 4 Enraf - Nonius diffractometer, available at the Sophisticated Analysis Instrument Facility (SAIF), IIT Madras, Chennai with Cu monochromatic radiation. This is a four circles diffractometer that can be used to do three different rotations of the crystal.

### 2.1.3 High Resolution X-ray diffractometry (HRXRD)

The multicrystal X-ray diffractometer designed, developed and fabricated at National Physical Laboratory (NPL), New Delhi was employed in the present investigations for high resolution XRD studies [4]. The schematic representation of this experimental set up is shown in figure 2.2. In this system a fine focus ($0.4 \text{ mm} \times 8 \text{ mm}$; 2 kW Mo) X-ray source energized by a well stabilized Philips X-ray generator (PW 1743) was employed. The X-ray source is combined with a long collimator, fitted with a pair of fine slit assemblies and a set of three (111) plane silicon
crystals for monochromating and collimating the exploring X-ray beam. The specimen forms the fourth crystal stage. The white X-ray beam first passes through a collimator and is then diffracted from two plane (111) silicon Bonse-Hart type [5] monochromator crystals. Well resolved MoKα₁ and MoKα₂ beams are obtained after diffraction from the crystals and a well collimated MoKα₁ beam is isolated and further diffracted from the third plane (111) silicon monochromator crystal, set in dispersive symmetrical Bragg geometry in (+,-,-). This arrangement improves the spectral purity (Δλ/λ << 10⁻⁵) of the MoKα₁ beam. Such an arrangement disperses the divergent part of the MoKα₁ beam away from the Bragg diffraction peak and thereby gives a good collimated and monochromatic MoKα₁ beam at the Bragg diffraction angle, which is used as an incident, or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+,-,-) and non-dispersive (+,-,+) configurations [6].

![Schematic diagram of multicrystal high resolution X-ray diffractometer](image)

**Fig.2.2** Schematic diagram of multicrystal high resolution X-ray diffractometer

When such a dispersive configuration is used, though the lattice constant of the monochromator crystal(s) and the specimen are different,
the dispersion-broadening in the diffraction curve of the specimen crystal does not arise. The specimen occupies the fourth crystal stage and is oriented for diffraction in (+,-,-, +) configuration. The height of the X-ray beam can be adjustable which is ~ 6 mm at the specimen stage with vertical divergence of ~10 arc minute in these experiments. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be << 3 arc sec. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.5 arc sec. The diffracted intensity is measured by using a scintillation counter, whose output is fed to a counting system (Philips, PW1749) built in a microprocessor-controlled unit used to give step wise rotations to the specimen through a stepping motor. The specimens were prepared by grinding and lapping and then chemically etched with suitable solvents.

2.2 Infrared spectrometry

The infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum to the microwave region [7-9]. IR regions of electromagnetic spectrum can be divided into three regions namely

1. near infrared region
2. mid infrared region and
3. far infrared region.

The region includes radiation at wavelengths between 0.7 and 500 μm or, in wave numbers, between 14000 and 20 cm⁻¹. The spectral range used most is the mid - infrared region, which covers frequencies from 4000 to 200 cm⁻¹ (2.5 to 50 μm). Infrared spectrometry involves examination of the twisting, bending, rotating and vibrational motions of atoms in a molecule. Near infrared region meets the visible region at about 12,500 cm⁻¹ and extends to about 400 cm⁻¹ (2.5 μm). Near IR spectrometry is a valuable tool for analyzing mixtures of aromatic
amines. NIR reflectance spectra find wide application in the tool and grain industry for the determination of protein, fat, moisture, sugar, oils, iodine numbers and so on [7-9].

**Mid infrared region**

Many useful correlations have been found in the mid IR region. This region is divided into the group frequency regions, (4000-1300 cm⁻¹) and fingerprint region 1350 - 650 cm⁻¹. In the group frequency region the principal absorption bands are assigned to vibration units consisting of only two atoms of molecule or functional group gives the absorption. The intermediate frequency range 2500-1540 cm⁻¹ is called unsaturated region. Triple bonds and double bonds appear in this region. The major factors in the spectrum between 1300 cm⁻¹ and 650 cm⁻¹ are single bond stretching frequencies and bending vibrations of polyatomic systems that involve motions of bands linking a substituent group of the molecule. This region is fingerprint region [4-6].

**Far IR region**

The region 650 – 50 cm⁻¹ contains the bending vibrations of carbon, nitrogen oxygen and fluorine with atoms heavier than mass 19. This low frequency region is sensitive to changes in the overall structure of the molecule. This region is sensitive to organometallic compounds or coordination compounds [7-9].

Infrared radiation can be analyzed by means of a scanning Michelson interferometer (Figure 2.3). Light from the source is split into two beams. One of the beams is passed through the sample under examination and is called the sample beam. The other beam is called the reference beam. When the beam passes through the sample it becomes less intense due to the absorption of certain frequencies. Now there will be a difference in the intensities of the two beams Let Io be intensity of the reference beam and I be intensity of the beam after interaction with the sample respectively. The transmittance (T=I/Io) of the sample at a
Experimental Techniques

particular frequency can be calculated. Intensities of the bands can be recorded as a linear function $T$ against the corresponding wave number. Intensities of the two beams are converted into and measured as electrical energies with the help of detector thermopile.

![Fig. 2.3 Schematic representation of FTIR spectrometer](image)

Fig. 2.3 Schematic representation of FTIR spectrometer

The two beams are made to fall on a segmented mirror $M$ with the help of two mirrors $M_1$ and $M_2$. The chopper ($M$) which rotates at a definite speed reflects the sample and reference beams to a monochromator grating ($B$). As the grating rotates slowly, it sends individual frequencies to detector thermopile which converts Infrared energy into electrical energy. It is then amplified with the help of amplifier ($A$). Due to the difference in intensities of the two beams alternating current start flowing from the detector thermopile to the amplifier. The amplifier is coupled to a small motor ($E$) which drives an optical wedge ($F$). The movement of the wedge is in turn coupled to a pen recorder which draws absorption bands on the calibrated chart. The movement of the wedge continues till the detector receives light of equal intensity from the sample and the reference beams.

2.2.1 Sample Handling

IR spectra may be obtained for gases, liquids, or solids.
Gases and Liquids

The spectra of gases or low boiling liquids may be obtained by expansion of the sample into evacuated cell. Cells equipped with freeze out tips are used for sample concentration and cell evacuation prior to the expansion of the sample into the cell. Liquids may be examined in solution. Neat liquids are examined between salt plates without spacer. Pressing a liquid sample between flat surfaces produces a film of thickness of 0.01 mm or less in thickness.

Solids

Solids are generally examined as a mull, a pressed pellet disc or as a deposited glass film. Mulls are prepared by thoroughly grinding 2-5 mg of a solid in a smooth agate mortar with 1-2 drops of mulling oil. Suspended particles must be less than 2 μm to avoid excessive scattering. The mull is examined as a thin film between flat salt plates nujol is commonly used.

Pellet technique

The pellet technique involves mixing finely ground sample (1-100μm) with potassium bromide powder and pressing the mixture in an evacuable die at sufficient pressure to produce a transparent disc. Grinding and mixing are done in a vibrating ball mill, other alkali halides are also used. The quality of the spectrum depends on the intimacy of mixing and the reduction of suspended particles size [9].

2.3 UV-vis- NIR spectrophotometry

A spectrophotometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus, the instrument compares the intensity of the transmitted light with that of the incident light.
The modern ultra-violet-visible spectrometers consist of light source, monochromator, detector, amplifier and the recording devices. The most suitable sources of light are: Tungsten filament lamp and hydrogen-deuterium discharge lamp which cover the whole of the UV-visible region. Tungsten filament lamp is particularly rich in red radiations i.e. radiations with wavelength 375 m\(\mu\), while the deuterium discharge lamp covers the region below it. The intensity of the deuterium discharge source falls above 360 m\(\mu\). The single source is found satisfactory over the entire UV-vis region. Ordinary spectrometers cover a range 220-800 m\(\mu\). Better instruments cover up to a short wavelength range of 185 m\(\mu\). This spectroscopic technique is not useful below 200 m\(\mu\) (inaccessible region) since oxygen absorbs strongly at 200 m\(\mu\) and below. To study absorption below 200 m\(\mu\), the whole path length is evacuated. The region below 200 m\(\mu\) is called vacuum ultra violet region. The low wavelength region can be extended upto 150 m\(\mu\) by flushing the instrument with nitrogen which absorbs below 150 m\(\mu\). Most spectrophotometers are double beam instruments. The primary source of light is divided into two beams of equal intensity. Before dividing it into two beams, the incident radiation is dispersed with the help of a rotating prism. The various wavelengths of light source are separated with a prism and then selected by the slits such that the rotation of the prism causes a series of continuously increasing wavelengths to pass through the slits for recording purposes. The selected beam is monochromatic which is then divided into two beams of equal intensity. Dispersion grating can also be employed to obtain monochromatic beam of light from poly chromatic radiation (UV-vis radiation). As the dispersion of a single beam or grating is very small, it is not possible to isolate or collimate very narrow band widths. Thus, light from the first dispersion is passed through a slit and then sent to the second dispersion. After the second dispersion, light passes through the exit slit. The main advantage of the second dispersion is that the band width of the emergent light increases and the light passing through the exit slit is almost monochromatic. Also most of the stray light is suppressed.
Fig. 2.4 shows the UV-vis- NIR Spectrophotometer. One of the beams of selected monochromatic light is passed through the sample solution and the other beam of equal intensity is passed through the reference solvent. The solvent as well as the solution of the sample may be contained in cells made of a material which is transparent throughout the region under study. Glass cannot be used since it absorbs strongly in the ultra violet region. Silica cells can be used. These must be properly stored and their optical surfaces should never be handled. Quartz cells also serve the purpose best. Glass can be used satisfactorily in the visible region [10]. After the beam pass through the sample cell as well as the reference cell, the intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument. The spectrometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution. Hence the effects due to the absorption of light by the solvent are minimized. In this way the absorbance or the transmittance characteristic of the compound alone can be measured. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotted as absorbance (A) against wavelength (λ).

![UV-vis- NIR Spectrophotometer Diagram]

**Fig 2.4 UV-vis- NIR Spectrophotometer**
When the sample absorbs light its intensity is lowered. Thus the photoelectric cells $P_1$ and $P_2$ will receive an intense beam from the reference cell and a weak beam from the sample cell. This results in the generation of pulsating or alternating currents which flow from the photoelectric cells to the electronic amplifier. The amplifier is coupled to a small servomotor which in turn is coupled to a pen recorder. Thus it records the absorption automatically.

2.4 Thermal analysis

Thermal analysis comprises several techniques in which physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme. When a material is heated or cooled, its structure and chemical composition can undergo changes such as fusion, melting, crystallization, oxidation, decomposition, reaction, transition, expansion and sintering. These changes can be observed by thermal analysis.

2.4.1 Thermogravimetry

Thermogravimetric analysis (TGA) or thermogravimetry (TG) provides a quantitative measurement of any weight changes associated with thermally induced transitions. It can record directly the loss in weight as a function of temperature or time for transitions that involve dehydration or decomposition. Thermogravimetric characteristic curves of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The rates of these thermally induced processes are often a function of molecular structure. Changes in weight results from physical and chemical bonds forming and breaking at elevated temperatures. These processes may evolve volatile products or form reaction products that result in a change in weight of the sample. The usual temperature range for TG is from ambient to 1200 °C in either inert or reactive atmospheres.
Samples are placed in a crucible that is positioned in a furnace on a quartz beam attached to an automatic recording balance. Fig 2.5 shows a TG instrument that contains a taut band suspension electromechanical transducer. The horizontal quartz beam is maintained in the null position by the current flowing through the transducer coil of an electromagnetic balance. A pair of photosensitive diodes acts as a position sensor to determine the movement of the beam. Any change in the weight of the sample causes a deflection of the beam which is sensed by one of the photodiodes. The beam is then restored to the original null position by a feed back current sent from the photodiodes to the coil of the balance. The current is proportional to the change in weight of the sample.

**2.4.2 Differential thermal analysis**

Differential thermal analysis measures the temperature, direction and magnitude of thermally induced transitions in a material by heating or cooling a sample and comparing its temperature to the temperature of
an inert reference material under similar conditions. This difference in temperature is determined as a function of time or temperature in a controlled atmosphere and provides useful information about the temperatures, thermodynamics and kinetics of reactions. This technique is sensitive to endothermic or exothermic processes including phase transitions, dehydration, decomposition and solid state reactions. A plot of the differential temperature ($\Delta T$), versus the programmed temperature ($T$), indicates the transition temperature(s) and whether the transition is exothermic or endothermic.

It consists of balance, furnace and sample carrier. The system was first evacuated with a diaphragm pump and then evacuated to $2 \times 10^{-4}$ m bar with turbomolecular drag pump both through port 4. Then the system was filled with standard grade argon or oxygen gas until reaching atmospheric pressure and the top valve (port 1) was opened to allow a constant flow of purge gas through the sample chamber. A 20 ml/min and 10ml/min flow were set through ports 2 and 3 for the balance protection and sample purge. A series of aluminum oxide plates were inserted at the base of the sample carrier to prevent radiation effects on the balance and to create a homogeneous gas flow through the furnace. A platinum sample carrier and platinum crucibles were used to allow temperature measurements in the higher temperature range without radiation effects. A heating cycle is programmed into the operating computer and a control system monitors and adjusts the furnace power to control sample and reference temperatures. The base line correction generated for each set of crucibles and heating rate. The base line correction is generated by running a specific heating program with an empty sample and reference crucible. The combined TG-DTA /DSC system is shown in Fig. 2.6. The furnace contains a block with identical and symmetrically located chambers. Fig. 2.7 shows the sample carrier and reference crucible.
The sample is placed in one chamber and a reference material, such as Al₂O₃ is placed in the other chamber. A thermocouple is inserted into the center of the material in each chamber. The furnace and sample blocks are then heated by a microprocessor controlled heating element. The difference in temperature between sample and reference thermocouples, connected in series opposition, is continuously measured. After amplification by a high gain, low noise dc amplifier for microvolt level signals, the difference signals is recorded as the y-axis. The temperature of the furnace is measured by an independent thermocouple and recorded as the x-axis. Because the thermocouple is placed in direct contact with the sample, DTA provides the highest thermometric accuracy of all thermal methods. DTA can be used in the temperature range from -190 to 1600 °C.
2.4.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) has become the most widely used thermal analysis technique. In this technique, the sample and reference materials are subjected to a precisely programmed temperature change. When a thermal transition (a chemical or physical change that results in the emission or absorption of heat) occurs in the sample, thermal energy is added to either the sample or the reference containers in order to maintain both the sample and reference at the same temperature. Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy. Since DSC can measure directly both the temperature and enthalpy for a transition or the heat of a reaction, it is often substituted for differential thermal analysis as a means of determining these quantities except in certain high temperature applications [11].

Cross section of a typical DSC cell is shown in Fig. 2.8. A DSC cell uses a constantan (Cu-Ni) disk as the primary means of transferring heat.
to the sample and reference positions and also as one element of the temperature sensing thermoelectric junction. The sample and reference are placed in separate pans that sit on raised platforms on the disk. Heat is transferred to the sample and reference through the disk. The differential heat flow to the sample and reference is monitored by the chromel/constantan thermocouples formed by the junction of the constantan disk and the chromel wafer covering the underside of each platform. Chromel and alumel wires connected to the underside of the wafers form a chromel / alumel thermocouple, which is used to directly monitor the sample temperature. Constant calorimetric sensitivity is maintained by the computer software, which linearizes the cell calibration coefficient. DSC provides maximum calorimetric accuracy from -170 to 750 °C. Sample sizes range from 0.1 to 100 mg.

![DSC cell cross section](image)

**Fig. 2.8** DSC cell cross section

### 2.5 Powder second harmonic generation efficiency study

The basic configuration used for the study of second harmonic generation in powders is shown in Fig. 2.9. It consists of a Q - switched laser whose beam falls unfocussed on to a thin section (0.2 mm) of powder of the material under study. After the fundamental beam is removed by a series of short wavelength passing filters, the second
harmonic is detected by a photomultiplier and displayed on an oscilloscope. A reference beam is obtained by use of beam splitter placed ahead of the sample. This enables the intensity of the fundamental or Q-SWITCHED LASER of 1.064 μm.

![Diagram](Q-SWITCHED LASER -> RCA 925 PHOTOTUBE -> TEXTRONIX 555 -> HV SUPPLY)

**Fig. 2.9** Basic configuration for powder second harmonic generation efficiency

second harmonic generated in a reference sample to be monitored by displaying both signals simultaneously on a dual beam scope. The system also permitted the insertion of narrow pass filters at the second harmonic wavelength between the shott filters and the photomultiplier to eliminate spurious signals [12].

**Sample preparation and Mounting**

Powders were made from single crystals using a Spex vibrating ball mill, and then graded using standard sieves. Particle sizes were checked by standard optical microscopy techniques. A thin layer (0.2mm) of
ungraded powder was placed on a microscope slide and held in place with transparent tape. For quantitative work powders were graded by using standard sieves to the desired range of particle sizes (about 75 to 150μ).

2.6 Microhardness

Hardness of a material is the resistance it offers to indentation by a much harder body. It may be termed as a measure of the resistance against lattice destruction or the resistance offered to permanent deformation or damage [13]. As the hardness properties are basically related to the crystal structure of the material and its bond strength, microhardness studies have been applied to understand the plasticity of the crystals [14].

It also facilitates to study the behavior of dislocations when the crystal is subjected to a stress. It is a technique for subjecting a crystal to relatively high pressure within a localized area. By suitable choice of indenter material and relatively simple equipment construction, hardness tests can be easily applied to all crystalline materials under various conditions of temperature and pressure. Deformation is local, so that a number of trials can be made on a single specimen of small dimensions and can be reproduced by maintaining the specimen indenter orientation relationship. Specimen of flat and relatively smooth surface is required.

2.6.1 METHODS OF HARDNESS TEST

Hardness measurement can be carried out by various methods. They are classified as follows.

1. Static indentation test
2. Dynamic indentation test
3. Scratch test
4. Rebound test
5. Abrasion test
The most popular and simplest form is the static indentation test wherein an indenter specific geometry is pressed into the surface of a test specimen under a known load. The indenter may be ball or diamond cone or diamond pyramid. Upon removal of the indenter, a permanent impression is retained in the specimen. The hardness is calculated from the area or the depth of indentation produced. The variables are the type of the indenter or load. The indenter is made up of a very hard material to prevent its deformation by the test piece so that it can cover materials over a wide range of hardness. For this reason either a hardened steel sphere or a diamond pyramid or cone is employed. A pyramid also has the advantage that geometrically similar impressions are obtained at different loads. So naturally a pyramid indenter is preferred. In this static indentation test the indenter is pressed perpendicularly in the surface of a sample by means of an applied load. Then by measuring the cross sectional area or the depth of the indentation and knowing the applied load an empirical hardness number may be calculated. This procedure is followed by Brinell, Meyer, Vickers, Knoop and Rockwell test [15-17].

In the dynamic indentation test, a ball or a cone (or a number of small spheres) is allowed to fall from a definite height and the hardness number is obtained from the dimensions of the indentation and the energy of impact.

The scratch test can be classified into two types:

(i) Comparison test in which one material is said to be harder than another if the second material is scratched by the first.

(ii) A scratch test with a diamond indenter on the surface at a steady rate and under a definite load. The hardness number is expressed in terms of the width of depth of the groove formed.

In the rebound test, an object of standard mass and dimensions is bounced from the test surface and the height of rebound is taken as the measure of hardness. In abrasion test, a specimen is loaded against a rotating disk and the rate of wear is taken as a measure of hardness.
2.6.2 VICKERS TEST

Among the various methods of hardness measurements discussed above, the most common and reliable method is the Vickers hardness test method. In this method, microindentation is made on the surface of a specimen with the help of diamond indenter (Fig. 2.10). Smith and Sandland [18] have proposed that a pyramid be substituted for a ball in order to provide geometrical similitude under different values of load. The Vickers pyramid indenter where opposite faces contain an angle ($\alpha = 136^\circ$) is most widely accepted pyramid indenter. A pyramid is suited for hardness tests due to the following two reasons

(i) the contact pressure for a pyramid indenter is independent of indent size and
(ii) pyramid indenters are less affected by elastic release than other indenters.

The base of the Vickers pyramid is a square and the depth of indentation corresponds to $1/7^{th}$ of the indentation diagonal. Hardness is generally defined as the ratio of the load applied to the surface area of the indentation. The Vickers hardness number ($H_v$) is defined as

$$H_v = \frac{2P \sin\left(\frac{\alpha}{2}\right)}{d^2} \ \text{kg/mm}^2$$

(2.2)

where $\alpha$ is the apex angle of the indenter ($\alpha = 136^\circ$). The Vickers hardness number is therefore calculated from the relation

$$H_v = \frac{1.8544}{d^2} \ \text{kg/mm}^2$$

(2.3)
Fig. 2.10 Schematic diagram of Vickers diamond pyramid indenter and indentation produced.

where \( P \) is the applied load in kg and \( d \) is the diagonal length of the indentation mark in mm. Hardness values are measured from the observed size of the impression remaining after a loaded indenter has penetrated and has been removed from the surface. Thus the observed hardness behavior in the final measurement of the residual impression is the summation of a number of effects involved in the materials response to the indentation pressure during loading.

The variation of Hv with applied indentation test load shows that with the increase of applied indentation test load Hv decreases at the low load region, reaching a saturation value at higher loads. Such phenomenon referred to as the indentation size effect (ISE). In order to describe the ISE behavior of materials several models for the relationship between applied indentation test load and indentation diagonal length have been reported in the literature (19). The most common explanation of the ISE found in the literature is directly related to the intrinsic structural factors of the test material. According to this theory in order to analyze the ISE in the hardness testing one needs to fit the experimental
data according to Meyer's Power law [20], which correlates the applied load $P$ and the resulting indentation size $d$ with each other.

$$P = Ad^n$$  \hspace{1cm} (2.4)

Where $n$ is the Meyer index or work hardening exponent and $A$ is constant for a given material. These parameters are derived from the curve fitting of experimental results of indentations. Combining equation (2.3) and (2.4)

$$H_v = Bd^{n-2}$$  \hspace{1cm} (2.5)

From this relation it is clear that for the ISE the values of $n$ should be less than 2. Note that the ISE is usually related to the deviation of the $n$ value from 2 for $n$ equal to 2 is the absence of an ISE [20]. The Meyer's law is simply an empirical expression to describing the relationship between indentation load and the resultant indentation size. It gives suitable results only in a narrow range of indentation loads. The Meyer's parameters were used for the characterization of the experimental data; however it was found that the classical Meyer's law is insufficient for the description of our experimental data. It is more suitable to use a polynomial equation for representation of experimental data. Recently a number of [13, 21, 22] workers explain the indentation size effect with the proportional specimen resistance (PSR) model. According to the PSR [19] model, there are two factors which are responsible for the decrease of microhardness with load. These are (i) the frictional force between the test specimen and the indenter facets and (ii) the elastic resistance of the test specimen. In the PSR model of Li and Bradt, microhardness can be described by two different parts: (i) the indentation load dependent part or the ISE regime and (ii) the indentation load independent part. The indentation test load $P$ is related to the indentation size $d$ as follows:

$$P = ad + a_d^2$$  \hspace{1cm} (2.6)
and equation 2.6 can be transformed into:

\[
\frac{P}{d} = a_i + \left[\frac{P_o}{d^2}\right] d
\] (2.7)

In equation 2.6 co-efficient \( a_i \) is the contribution of proportional specimen resistance to the apparent microhardness and \( a_i \) is a co-efficient related to load independent microhardness. \( P_o \) is the applied load at which microhardness becomes load independent and \( d^2 \) is the corresponding diagonal length of indentation. The parameters \( a_i \) and \( P_o/d^2 \) are included in equation and can be evaluated through the linear regression of \( P/d \) versus \( d \). A plot of \( P/d \) against \( d \) will give a straight line, the slope of which gives the value \( P_o/d^2 \). The load independent microhardness value can be calculated by multiplying \( P_o/d^2 \) with the Vickers conversion factor 1.8544.

\[
H_v = 1.8544 \times \frac{P_o}{d^2} \text{ kg/mm}^2
\] (2.8)

### 2.7 Dielectric constant

When a dielectric material is subjected to an electric field the net polarization of the medium is altered. The dielectric constant and dielectric loss may be obtained from a measurement of the real and complex admittance of a crystal. These measurements are particularly straightforward with impedance bridges which separate the conductance and capacitance of the crystals. Unpoled crystal has been used for this measurement and this is mainly used for the identification of phase transitions and the recording of transition temperatures [23].

#### 2.7.1 Experimental set up

A two terminal sample holder was used for dielectric measurements. The cell was made of copper and the sample was held
between the electrodes to ensure proper electrical contact at all temperatures. The sample cell was placed in a thick cylindrical aluminium block. The large thermal capacity so achieved by this arrangement gave a good thermal insulation to the cell and helped in making the temperature variation of the cell very slow with time and the entire sample had uniform temperature. A thermocouple was fixed in the vicinity of lower electrode to measure the temperature of the sample. In the present study, the sample holder was heated at slow rate from room temperature to 10 °C above the transition temperature. The temperature of the sample was allowed to stabilize for few minutes and subsequently capacitance values were recorded for different frequencies from 40 Hz to 100 KHz with an ac field of 1V/cm. Hewlett Packard Low Frequency Impedance Analyzer (Model HP 4192A) was used for this measurement. The dielectric constant was calculated using the relation

\[ \varepsilon' = \frac{Ct}{(\varepsilon \cdot A)} \] (2.9)

where \( C \) is the capacitance, \( t \) the thickness of the dielectric, \( \varepsilon \) the permittivity of free space and \( A \) the area of the capacitor.

**References**


