Chapter 2
CHARACTERIZATION TECHNIQUES

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CHAPTER 2
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2.1 Introduction

Crystals are grown mainly for two purposes; (1) to understand how crystals are grown and (2) for scientific and technological uses. For either of these purposes one must evaluate the quality of the grown crystals (Laudise 1972). To understand how crystal growth process influence perfection or to produce crystals of the perfection required, one must determine the nature and number of imperfections in grown crystals. Therefore, a crystal grower should be intimately involved with the assessment of the grown crystals. The assessment of the physical and chemical perfection of materials is called characterization (Kane, 1970). Full characterization of a crystal includes the determination of the nature, concentration and distribution of all impurities and defects. A whole spectrum of techniques from exotic physical methods to classical analytical chemistry is employed in characterizing a material which does not mean the measurement of user oriented properties alone. Thus while a solid state physicist should aim at measuring properties of interest for physical theory or device performance, it remains for a crystal grower to correlate these
properties. Further, these measurements are to be supplemented with analytical, chemical and other physical instrumental measurements. Of the many physical methods involved the most important are the X-ray diffraction and spectroscopic methods which include Atomic absorption spectrometry, IR, mass spectrometry, UV-visible spectroscopy, ESR, NMR, Mossbauer and neutron activation analysis. The choice of the method to study the nature of a material depends very much upon the crystallinity of the specimen and availability of equipment.

2.2 Optical microscopy

There are several approaches to the study of surfaces but a geometrical or structural investigation will be the most fundamental one. Modern microscopy plays an important role for such studies. The progress in modern optical microscopy has been accelerated since the discovery of phase contrast in 1934. Now, we have easy access to versatile modern microscopy since phase contrast and differential interference microscopes are being employed for observing surface topography (Richardson, 1971).

It was in the early 1920’s that crystal faces were studied in detail for the first time. The second high tide of surface micro-topographic studies came when Griffith found spirals which lead to Frank’s spiral growth theory. This was followed by a vast number of observations on a wide variety of crystals by Verma and Amelinckx which provided further evidence. These were supported by the development of precise optical methods.
Since both macro-morphology and micro-morphology of crystals are determined by two factors ie structural and environmental, we can obtain both types of information in addition to information relating to the growth and dissolution process of crystals. Surface morphology is not only an indicator of internal crystal perfection but it also performs the link between this perfection and growth conditions. But surface microtopographs of crystal faces represents only the final stages of crystal growth. It is therefore advisable to combine surface microtopographic studies and observations on internal bindings, sector structures, dislocation bundles etc. These may be detected by etching methods, polarization or infrared microscopes, X-ray topographic methods etc.

Optical microscopy can be employed for revealing structural information. If crystals grow under a near equilibrium condition their external forms will be equilibrium forms defined by structural factors. The micro morphology of growth spirals will reflect structural characteristics. Mostly the morphology of growth spirals of monomolecular height reflect the structural characters of the face very vividly. Another important feature is that macro morphology follows the symmetry elements of the crystal while micromorphology follows the symmetrical elements of the face.

### 2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) is considered to be a very effective scientific tool in studying crystal surfaces both microscopic and macroscopic. With an increasing technological level and decreasing dimensions of structures, the necessity for the use of electron microscopical methods with higher
resolving power was growing. SEM can be employed for studying the mechanical stability of solids containing cracks and crack like defects, thus leading to investigation of real structure of solids. In crystalline solids when temperature is not too high compared to melting temperature, plastic deformation takes place as a crystallographic slip. Consequently steps are formed on the crystal surfaces which can be imaged and quantitatively evaluated by electron microscope surface techniques (Friedel, 1964). From SEM, one can effectively build up a relationship between the microscopic parameters of dislocation processes and macroscopic deformation. Surface effects have to be considered generally if bulk properties are to be derived from surface investigations.

Another use of SEM is that, based on its observations the microscopic deformations as well as fracture behavior can be related to microprocess of flow and rupture. For crystalline solids the microcracks generate local plastic deformation. These defects decisively influence the fracture strength in crystalline solids. The density and length of microcracks can be measured by SEM. Thus electron microscopic methods contribute much to the knowledge of crystal plasticity. The dislocation structure generated by the deformation reveals much detail for numerous crystalline materials (Hirsch et al., 1965; Martin, 1978). SEM fractography reveals high speed microprocesses taking place during fast crack propagation leaving markings on the fracture surface.
2. Characterization technique

2.4 Infrared spectroscopy

IR spectroscopy has been widely used in the characterization of a large number of organic and inorganic crystals. Absorption of IR energy by a substance is associated with the vibrational and rotational motion of molecules within it. Commonly it employs the group vibrational concept to ascertain the presence or absence of various functional groups in the molecule. Certain chemical groups have characteristic absorption bands consistent among minerals containing these groups. The spectra originate primarily from vibrational stretching and bending modes within molecules. This method offers a fingerprint for identification of molecular structures. Empirical correlations of vibrational groups with specific observed absorption bands offer the possibility of chemical identification and possibly quantitative analysis through intensity measurements (Sachinath Mitra, 1989).

The IR region of the electromagnetic spectrum extends from red end of visible region up to microwave region (14000–20 cm$^{-1}$). Upon interaction with infrared radiation the molecules of a substance absorb the portions of the incident radiation at a particular wavelength (Allinger and Allinger 1988). The function of an IR instrument is to irradiate a sample with infrared radiation and measure the degree which the sample absorbs it. Multiplicity of vibrations occurring simultaneously produces an absorption spectrum characteristic of the functional groups and overall configuration of the atoms of a molecule. Most organic molecules contain a number of carbon atoms bound together and their motions couple in complicated ways. Coupling is usually strongest between vibrations of similar frequency. Due to the small mass of hydrogen the C-H
stretching and C-C stretching motions are of very different frequencies and do not couple to any extent. However other motions of the hydrogen in a hydrocarbon are possible (Braun 1987). The result is a very complex pattern of bands in the spectra of most organic molecules in the region of 1400-800 cm\(^{-1}\). Much of this pattern is a function of the total skeleton and this part of the spectrum is referred to as the finger print region. This region is a characteristic of a certain molecule.

For qualitative analysis one of the best features of an IR spectrum is that the absorption or lack of absorption in specific frequency regions can be correlated with specific stretching and bending motions. Thus from the interpretation of the spectra one can state whether certain functional groups are present or not.

IR spectroscopy is sensitive to changes in the dipole moments of vibrating groups in molecules. Advances in technology have lead to the development of FTIR which provides improved spectra for interpretation. In the present work the IR spectra of the samples grown were recorded in KBr pellets using a Perkin Elmer IR spectrophotometer Model 283.

2.5 X-ray diffraction analysis

In recent years the numerous and varied applications of XRD have established it as one of the most fundamental and important research tools. It is a basic scientific tool capable of supplying the investigator with fundamental
data and information unobtainable by any other technique. The most widely used diffraction procedures are those applied to poly crystalline material (Winchel and Winchel, 1964; Sachinatumitra, 1989).

The phenomena of XRD by crystals results from a scattering process in which x-rays are scattered by constituent atoms without change in wavelength. The resulting diffraction pattern of a crystal comprising both the positions and intensities is a fundamental physical property of the substance serving not only for its speedy identification but also for complete structural elucidation. Further analysis leads to a knowledge of the size, shape and orientation of the unit cell.

Out of the various possible XRD methods the powder method is of special importance since it is the only technique which is readily applicable to all crystalline materials. Diffraction data depends on the lattice parameters which are unique for one particular material and can be employed for proper identification purposes (Klug and Alexander 1962). From the diffraction pattern we can get the interplanar spacing of the reflection, miller indices, unit cell dimensions, lattice type, intensities of reflections, crystallite size from line broadening, lattice constant etc. (Lipson and Steeple, 1970). Data cards which are available provide the most efficient application of powder diffraction and are accepted universally as standard reference for analysis.

An important advantage of XRD over other methods is that the results obtained are in terms of materials as they occurs in the samples and not in terms of elements or ions present. It is often the only satisfactory method of distinguishing among polymorphs or detecting a compound in the presence of
others containing the same element. When used in conjunction with other methods like electron diffraction, EDS, TEM etc, XRD proves effective in distinguishing any two crystal phases.

A powder pattern is obtained when X-rays are diffracted by a sample consisting of a very large number of randomly oriented crystalline particles, ie a powder sample. The position of reflected beam is governed by Bragg’s law.

\[ 2d_{hkl} \sin \theta_{hkl} = \lambda \] (2.1)

For any given combination of indices hkl, all reflections from the powder lie on a cone of semivertical angle \( \theta_{hkl} \). If \( a, b, c, \alpha, \beta \) and \( \gamma \) are the details of the unit cell, the values of \( \sin^2 \theta_{hkl} \) for the various crystal systems are (Lipson and Steeple, 1970).

1. Cubic system

\[ \sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \] (2.2)

2. Tetragonal system

\[ \sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2} (h^2 + k^2) + \frac{\lambda^2}{4c^2} l^2 \] (2.3)

3. Hexagonal system

\[ \sin^2 \theta_{hkl} = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{4c^2} l^2 \] (2.4)
4. Orthorhombic system

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2} h^2 + \frac{\lambda^2}{4b^2} k^2 + \frac{\lambda^2}{4c^2} l^2$$  \hspace{1cm} (2.5)$$

5. Monoclinic system

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \frac{h^2/a^2 + k^2/c^2 - 2hk/ac \cos \beta + k^2/b^2}{\sin^2 \beta}$$  \hspace{1cm} (2.6)$$

6. Triclinic crystal

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \frac{\frac{h^2 \sin^2 \alpha}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2 \sin^2 \gamma}{c^2}}{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma + \frac{2hk[\cos \alpha \cos \beta - \cos \gamma]}{ab} + \frac{2kl[\cos \beta \cos \gamma - \cos \alpha]}{bc} + \frac{2lh[\cos \gamma \cos \alpha - \cos \beta]}{ca}}$$  \hspace{1cm} (2.7)$$

where \( \alpha, \beta, \gamma \) are the angles between \( b \) and \( c \), \( c \) and \( a \), and \( a \) and \( b \) respectively. Equations for the triclinic system can be simplified when expressed in terms of the unit cell in reciprocal lattice (RL): \( a^*, b^*, c^*, \alpha^*, \beta^* \) and \( \gamma^* \) specify a RL.

$$a^* = \frac{1}{a}, \quad b^* = \frac{1}{b}, \quad c^* = \frac{1}{c}$$

for the monoclinic system,

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \left( h^2 a^* b^* + k^2 b^* c^* + l^2 c^* a^* + 2lh c^* a^* \cos \beta^* \right)$$  \hspace{1cm} (2.8)$$
and for the triclinic system,

\[ \sin^2 \theta_{hkl} = \frac{\lambda^2}{4} (h^2 a^* \cdot a^* + k^2 b^* \cdot b^* + l^2 c^* \cdot c^* + 2 h k b^* \cdot c^* \cos \alpha^* + 1) \]

(2.9)

Here again the values of \( \sin^2 \theta \) are calculated for all possible values of \( h, k \) and \( l \). Then they are compared directly with the values of \( \sin^2 \theta \) determined from the observed data.

In the present work the XRD patterns of the grown crystals were recorded in Philips X-ray diffractometer with wide angle goniometer PW1050/70 and proportional detector PW 1965/60 using CuK\( \alpha \) radiations in the 2\( \theta \) range 0 to 60\( ^0 \). The crystals are identified by comparing the interplanar spacing and intensities of the powder pattern to the pattern in the ASTM index file.

2.6 UV-visible spectroscopy

This technique enables structural information for characterization of crystals. UV spectroscopy is mainly used to detect conjugated systems because the promotion of electrons from ground state to the excited state of such systems would give rise to absorption in this region (Dudley, 1988). UV absorption usually corresponds to excitation of an electron from the ground state to a higher state. In most cases absorption occurs when a ground state electron in a
bonding or non bonding molecular orbital is excited by the incident radiation to a higher molecular orbital.

Since different chromophores have UV-visible absorptive maxima at different wavelengths, it is possible to identify the absorbing molecule by comparing the wavelength of the absorptive maximum with the spectrum of a sample of known substance. When a beam of specific wavelength impinges upon a substance, the energy associated with the beam may be altered by reflection, refraction absorption or transmission processes. In a scanning spectrophotometer a spectrum of absorbance, transmittance or log of absorbance as a function of wavelength can be obtained (Lambert, 1976). The simplest situation with respect to the intensity of absorption is that in which the system obeys the Lambert-Beer law. If $I_0$ is the intensity of a parallel beam of radiation incident normally on a layer of thickness $l$ cm and molar concentration $c$ and $I$ the intensity of the emergent beam then,

$$\log_{10} \frac{I_0}{I} = \varepsilon cl \quad (2.10)$$

$$A = \varepsilon cl \quad (2.11)$$

where $\varepsilon$ is the molar absorptivity (litre/mole/cm) is independent of $c$ but is a function of wavelength, temperature and nature of the solvent. $A$ gives the absorbance of the sample in the beam. Of course this implies that each layer, or indeed each molecule of the absorbing substance absorbs a constant fraction of the incident radiation.
In the present study UV absorption spectra of the grown crystals were recorded at room temperature using a ‘SHIMADZU UV-2100S’ UV visible recording spectrophotometer. Cells employed were of 1.0 cm in optical path.