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EXPERIMENTAL TECHNIQUES FOR CHARACTERISATION AND PROPERTY STUDIES OF CRYSTALS

3.1 Introduction

The characterisation and the studies of the properties of crystals of materials are very important, in the context of technological applications. These studies reveal the perfection of the crystals, influence of the methods on the growth of materials and identity of the grown material. Study of the crystal habit forms an important part as it influences the physical properties.

The past few decades have witnessed revolutionary advances in the methods of characterisation of materials. Some of the experimental methods of characterisation employed in the present work includes microtopography, dislocation studies, thermal analysis, X-ray diffraction techniques, UV-visible spectra, fluorescence or emission spectra, Energy dispersive analysis by X-rays (EDAX), TG-DTA techniques, etc. To study the magnetic property the author has used vibrating sample magnetometer (VSM) and to study the mechanical property of the crystal microhardness tester has

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been utilised. The principles involved in the measurements and salient features of the instruments are discussed in this chapter.

3.2 Optical microscopy

The grown crystals whether microscopic or macroscopic in size, optical microscopy is employed as a standard method to examine the growth habit of the crystal. The detailed studies of the surface of the crystal reveal the growth pattern and the occurrence of defects and impurities. There are several approaches to study the features of the surfaces. But a geometrical or structural investigation is one of the most fundamental aspects[1,2].

The powerful optical microscope, Lietz. Metallux-3, which although involves complicated operational features yet is a versatile instrument, was employed for the surface examination of the gel grown rare earth hydrogen selenite crystals. It is a binocular polarising microscope with versatile functions. The modupak AF can be used for the bright field, dark field, polarised light and phase contrast. It has a FSA20 binocular phototube with 30° viewing angle camera of adjustable inter papillary distance. In the vertical photo-port of the microscope, a camera is attached for photographing the image. The lamp housing can be adjusted for reflected or transmitted position along with the filters. The magnification of 50, 100, 200 and 1000 times are possible with the adjustable objectives. The microscope has adjustable resolution.

3.3 Etching studies

To investigate the perfection of the crystalline materials, etching studies are eminently suitable. The observation of the crystal surface after the etching reveals the growth pattern and perfection of the crystal to a good extent. Etching is the result of variations in surface reaction or dissolution rates, brought about by crystallographic orientation effects, lattice imperfection and chemical composition[3]. Crystalline defects such as grain boundaries, stacking faults, vacancy, dislocation and other surface features are revealed by etching[4].

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The etching method involving spontaneous chemical reaction between the solid and etchant is called chemical etching. Several formulations of etchat solutions and a large number of etching techniques exist in the literature. The selection of etchant and procedure of etching requires great expertise and experience. In the context of the selenite crystals HNO_3 (10-20%) is found to be a suitable etchant. The time of etching, concentration of etchant and the dimension of the crystal influence the etched patterns. After the etchant is used for a stipulated time, the sample is washed with water thoroughly to prevent further dissolution before investigation by high-resolution optical microscope. The etch pits and etch patterns observed through high-resolution optical microscope reveal the growth features and the origin of dislocations in the crystals. An experienced investigator can also identify the geometry of the domain walls by the help of the etch patterns.

3.4 X-ray diffraction Methods

The identity test of a crystal starts with the X-ray diffraction studies. The methods of X-ray diffraction to identify the crystal structure and determining the space group of the crystal are well documented[5,6]. Both single crystal and powder methods have been extensively used due to the simplicity of the method. The advent of high-resolution photon detectors and on-line computing has replaced the age-old photographic technique.

In the powder technique the crystal sample is in a finely powdered form, in which small crystals are oriented in every possible direction. When the X-ray penetrates through the material, a number of particles can be expected to be oriented in such a way as to fulfil the Bragg condition for reflection from every possible inter planar spacing.

In this work a fully computerised X-ray diffractometer (Rigaku) has been employed for the powder diffraction studies. Rigaku single crystal diffractometer is used for the single crystal structural studies. The source is a monochromatic Cu-Kα beam suitably filtered. The samples are held in the sample holder and placed on a wide-angle goniometer. The rotation of goniometer provides the randomness of the

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orientation of the crystal planes. The diffraction patterns obtained by automatic scanning are recorded by the computer. The measured intensity as a function of the angle is compared with standard ASTM data, which completes the identification of the crystal structure and space group.

3.5 FT-IR spectroscopy

This technique is one of the most important and widely used spectroscopic techniques of analysing quantitatively the structural units[7,8,9] of the unknown compound. The IR absorption rates of poly-atomic molecules comprise a range of $10cm^{-1}$ $12,800cm^{-1}$. IR absorption is due to the change in magnetic dipole moment of the molecule arising due to the relative vibrational motion of the negative and positive charges. IR spectroscopy is classified into three regions of the electromagnetic spectrum.

i. NIR (Near IR) (12000 – 4000) cm^{-1}
ii. MIR (Mid IR) (4000-200) cm^{-1}
iii. FIR (Far IR) (200 – 10)cm^{-1}

The mid IR ranges encompasses a vast amount of analytical applications. It provides a unique fingerprint of the molecules, which can be clearly distinguished from the absorption patterns of other vibrations. Conventionally there are two methods adopted for recording IR spectrum of the solid sample, one is the mull method and the other is KBr pellet method. The powdered sample is dispersed in the mulling agent made of 'metal oil' (nugol) and the slurry thus formed is placed in the spectrometer. The KBr pellet method is more popular and has several advantages over the mull method, such as low scattering loss, higher spectral resolution, the homogeneity of the sample etc. In this study the KBr pellet method was used to record the IR spectra of the hydrogen selenite crystals of rare earths. The weight of the sample required for the analysis is very small (~30mg).

In the present investigation, the Shimadzu FTIR-8101A spectrophotometer was used for the analysis. It consists of a source of IR radiation and a sensitive transducer. All

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absorption bands in the range $4000cm^{-1}$ to $200cm^{-1}$ can be recorded in the instrument with high resolution. The spectra obtained are compared with the standard data of the particular group of molecule.

3.6 Thermal analysis

3.6.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) measures changes in weight of a sample being heated. The weight is monitored in real time and changes, either gains or losses, are evident immediately. The apparatus consists of the sample situated within a crucible, which is enclosed within a temperature controlled furnace. The sample and crucible is counterbalanced on a sensitive analytical balance. Weight changes are directly plotted on a multi-pen recorder. Weight readout is usually accomplished by one of the two methods, a linear transducer or a capacitance change between two flat plates, one of which is free to move with the balance swing. A resistance capacitance tank circuit completes the electronics, producing a reasonable voltage[10].

A SETRAM-92 TG-DTA instrument has been used for the present study. The temperature range selected for the study was from ambient to 1100°C. Argon was used as the inert atmosphere to purge the furnace and prevent oxidation of the sample. The thermocouple is placed very close to the sample container to record temperature. The computerised temperature control system compares the voltage output in the thermocouple with a voltage verse temperature table, which is stored in the ROM. The balance measures the weight losses of the sample on heating and transfers the data to the computer. Clearly the thermogram contains sufficient data to calculate the weight of each of the element present in the sample during phase changes.

3.6.2 Differential thermal analysis (DTA)

A thermocouple is one of the important probes in the DTA instrument. The measure of change in heat flow is related to specific heat capacity (C_p). If we programme the temperature increase so that it rises in a perfectly linear manner, i.e. $dT/dt = k$, then

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the heat flow into both the reference and the sample will be constant. The most important parameter for DTA is a constant heat flow[10]. The parameters associated with DTA method are:

1. dT/dt = k
2. Sample size.
3. Rate of heating
4. Degree of crystallinity of sample.
5. Effect of external atmosphere.

The rate of heating generally used for most inorganic materials ranges between about 2° to 20°/minute, while that for organic compounds lies between about 15° to 100°/ minute. In the present work a heat flow at the rate of 10°/minute is used.

In general, solid state decomposition reactions occur as endothermic peaks (ΔH is negative and heat is absorbed) while phase changes, that is changes in structure, occur as exothermic peaks (ΔH is positive and heat is evolved).

3.7 Absorption and emission spectroscopy

3.7.1 UV-Visible absorption spectroscopy

This is one of the most important analytical methods in many chemical, biological and clinical laboratories. Most organic components and many inorganic ions and complexes absorb radiation in the UV-Visible region. From the observed spectra one could identify the presence of the particular elements in the spectra.

The ultraviolet and visible spectrum in a narrow region is of interest in the present work. Despite its narrowness, this band of radiation is vital to life on earth because its interaction with molecules is of primary importance in both photosynthesis and vision. Measurement of such molecular interactions forms the basis of UV-visible spectroscopy and can provide a wealth of information about the molecules. In the UV-visible region, wavelength is the appropriate parameter generally used for the analysis. The convenient unit of wavelength in this region is the nanometer. When

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frequency is used, it is generally expressed in terms of wave numbers, i.e. the number of waves per cm.

$$\lambda = 10^9 c/\nu = 10^7/\tilde{\nu}$$

Where λ is the wavelength in nanometer (nm), ν is the frequency in hertz, $\tilde{\nu}$ is the frequency in wave numbers (cm^{-1}) and c ms^{-1} is the velocity of light (2.998×10^8 ms^{-1})

The limits of the visible spectrum are ill defined, but are taken between 400nm and 800 nm. The UV region extends from 400nm to 100nm. The near infrared (NIR) is above 800nm. In the present work the regions of absorption spectrum recorded is in between 200 to 1100nm. A Shimadzu 160A spectrophotometer was used for the analysis.

The absorption of radiation occurs when UV-visible radiation encounters an atom or molecule, and interaction between the radiation and the electrons of the latter takes place. This absorption process is highly specific and results in an attenuation of radiation and an increase in the energy of the electron of the atom or molecule.

This may be regarded as the promotion of one of the outer or bonding electrons from a ground state energy level into one of higher energy levels. These levels are separated by a discrete energy increment E, which is determined by the nature of the atom or molecule, and only quanta of radiation of energy E can be absorbed. This quantum of energy is related to the frequency and wavelength of radiation by

$E = h\nu = hc/\lambda \times 10^9$, $h = 6.63 \times 10^{-34}$ JS

$c = 2.998 \times 10^8$ ms^{-1}, λ in.nm.

In the present study this technique has been utilised to find the presence of rare earth ion in the crystal and is thoroughly described; elsewhere.

3.7.2 Emission Spectrometry

Emission spectra are complementary to the absorption spectra. In this work the emission spectra have been recorded by a simple experimental set up. In this an

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excitation source is a fibre coupled nitrogen laser which can deliver pulses of duration 1 ns having an average power of 2.5 mw and frequency 100 Hz.

When the beam falls on the sample, the fluorescence emission takes place. The fluorescence emission due to the constituent rare earth ion in the crystal is identified with the help of the UV-visible absorption spectrum.

3.8 Energy dispersive analysis by X-rays (EDAX)

Energy dispersive analysis by X-rays is an important analytic technique used to determine the chemical composition of the elements present in the material. When a beam of high-energy electrons is incident on the specimen, its atoms are excited and while returning to the ground state they emit X-rays. The energy of the X-rays depends on the atomic number of the elements excited. Hence the constituent element present in the compound or crystal can be determined. The intensity of the emitted X-rays will be proportional to the concentration of the elements in the sample. The method is a non-destructive one and gives simultaneous record of all elements having $Z \geq 11$.

In the present study EDAX analysis of the samples has been carried out using a Link AM 10,000 instrument. The main component of an energy dispersive spectrophotometer consists of a polychromatic source, a sample holder and a detector. A lithium drifted silicon p-i-n diode held at liquid nitrogen temperature is used as the detector of the emitted X-rays. The cooled detector is covered by a beryllium window. The output pulses are stored in a multichannel analyser.

3.9 Microhardness measurements

To study the microhardness property of crystals the indentation technique has been employed. A Vickers micro hardness tester is employed for this purpose. The specimen (grown crystal) to be indented is mounted on a platform and a most planar region is selected by viewing through a microscope. The indenter button is then pressed during which time a red light glows till the end of the indenting. The indenting time is 20 seconds. After the completion of indentation, a yellow lamp

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glows. The position of indenter is observed through the microscope and measurements taken.

The diagonal of such indentation marks are measured and the Vickers hardness numerical (VHN) is calculated using the formula.[11]

$$VHN = (2\ P\ Sin\ \theta/2)/d^2\ \ kg\ mm^{-2}$$

Where P is the load applied on the in units of Kilogram weight (kW), θ is the angle between the opposite faces of the indenter and d is the average diagonal length in mm. For θ = 136°, as is the case with Vickers pyramidal indenter, the formula is

$$VHN = 1.85 \times P/d^2\ \ kg\ mm^{-2}$$

3.10 Magnetisation measurements (VSM)

A vibrating sample magnetometer (VSM) is a device in which the sample is vibrated in a uniform magnetising field and the magnetisation of the sample is detected.[12,13,14]. The precise measurements of magnetisation as a function of temperature, magnetic field strength and crystallographic orientations can be done by this instrument.

When the specimen is placed in a uniform magnetic field, a magnetisation is induced in the sample equal to the product of the susceptibility and the applied magnetic field. Due to the vibration of the sample, a sinusoidal motion begins and electrical signal due to the flux change can be induced in a stationary pick-up coil, placed in a suitable position. The electrical signal is proportional to the magnetic moment, amplitude of vibration and vibrational frequency.

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