CHAPTER 3
EXPERIMENTAL TECHNIQUES

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CHAPTER 3
EXPERIMENTAL TECHNIQUES

3.1 Introduction:-

Any crystal work is intimately involved with the assessment of the grown crystal. The assessment of chemical and physical perfection of the material can be done in laboratory has come to be called as characterization. The process of characterization describes feature of the composition and structure of the material. A wide variety of method of variable precision and dependability are available for the structure determination of the crystal. Morphology of the crystal depends on the different rate of growth of its faces in different crystallographic directions. During crystallization, one set of faces may be induced to grow faster than others or the growth of another set may be retarded. The size and shape are completely irrelevant being determined only by the accidental condition prevailing at the time of the information.

Crystal habit of various crystals, grown under different conditions and also by different methods are described by Buckley[1], Hartman [2], Kern [3], Chernor [4], Burton [5], and Mullin [6]. A number of factors such as degree of saturation, type of solvent, pH of the gel, presence of impurities which have been known to affect the morphology of the crystal studied by Well [7], Mullin [8], Pillai [9], Buckley[10] Nassu[11]. Change in growth temperature also presumably affects significantly the morphology which is predicated by Patel and Arora[12]. In present work Bismuth Iodate, Bismuth Iodide & Bismuth Trisulphide crystals grown with
changing different parameters. Nucleations of the crystals mostly occur at the top of gel. The number of nucleation decrease with the increase in distance from the gel solution interface and the size of the crystals also improved. Most of these crystals are bright and quite transparent.

The advanced of science and technology in the recent years has replaced the traditional and laborious experimental techniques of analysis by sophisticated instrumental techniques of analysis, which gives more accurate and reproducible results. Characterization of grown crystals involves the assessment of the crystal in terms of its structure, composition and properties. For characterizations of grown crystals, a large number of techniques are available. It is necessary to give brief account of the various techniques used in the present work. Important factors, which must be taken into account, when selecting an appropriate method of analysis are,

- Nature of the information, which is sought.
- The size of sample available and the portion of the constituents to be determined.
- The purpose for which the analytical data is required.

In the present work, grown crystals were characterized by following methods.

1. X-ray Diffraction (XRD)
2. Fourier Transform Infrared Spectroscopy (FTIR)
3. Thermal Analysis which includes
   - Thermal Gravimetric Analysis (TGA)
   - Differential Thermal Analysis (DTA)
3.2 X-ray Diffraction Studies (XRD) :-

XRD is the combined effect of scattering and interference of electromagnetic radiation. Radiation used for structure determination must have short wavelength one comparable with the inter-atomic distance. X-rays diffraction technique can therefore be used for structure determination.

The phenomenon of scattering from the basis of diffraction, when a beam of X-ray is incident upon a substance, the electron constituting the atoms of the substance become as small oscillators. These on oscillating at the same frequency as that of incident X-ray, emits electromagnetic radiations in all direction at the same frequency as the incident X-radiation. These scattered waves are coming from electrons, which are arranged in a regular manner in a crystal lattice and then traveling in certain direction. If these waves undergo constructive interference, they
are said to be diffracted by the crystal plane. Every crystalline substance scatters the X-ray in its own unique diffraction pattern, producing a fingerprint of its atomic and molecular structure.

The conditions of diffraction are governed by Bragg’s law and the diffracted beams are often referred to as reflection. Constructive interference of the reflected beam emerging from two different planes will take place if the difference in the path length of two rays is equal to whole number of wavelengths. This can be understood from fig 3.1. If one X-ray is striking the top crystal plane at A and the other X-ray is striking the second crystal plane at B, the path difference between the two parallel X-rays is equal to CB+BD. But for constructive interference,

\[ n\lambda = CB + BD \quad \text{but} \quad CB = BD = l \]

Therefore \[ n\lambda = l + l = 2l \]

But from \( \Delta ABC \), \[ l = d \sin \theta \]

The given wave can be reflected only if it satisfies the equation.

\[ n\lambda = 2d \sin \theta \]

Where, \( n \) – Integer

\( \lambda \) – Wavelength

\( d \) – Distance between adjacent planes

\( \theta \) – Glancing angle of incident and outgoing radiations

On putting the integer \( n = 1, 2, 3, \ldots \) etc, a series of angle is obtained at which reflection will occur for a given set of plane of spacing \( d \). These reflection are referred to as first order, second order, third order, respectively.
 Completely destructive or constructive interference occur in a specific direction which depends on:

- Spacing of atoms.
- Wavelength of incident radiation.

Bragg's considers the row of identical atoms as the plane. He showed that any diffracted ray can be regarded as if it were reflected from one of these systems of planes, much as though it were reflected from a mirror parallel to planes. Diffracted beams are found only when reflections from parallel planes of atoms interfere constructively. Here elastic scattering is considered. Inelastic scattering is accompanied by excitation of elastic waves in crystals.

This equation states that \( \theta \) has a unique value for a given set of crystal planes, a given \( n \) and a given \( \lambda \). Therefore, the incident wave of a given wavelength must strike the crystal in some direction which lies in a cone which makes a definite angle with a given set of planes. Conversely if the diffracted wave is observed, it may be conducted that the crystal possesses a set of planes with a normal in that direction which bisects the angle between the incident and diffracted waves.
This relation shows that, why radiation in X-ray region of spectrum are most useful for crystal analysis. The inter-atomic spacing of solid is about 2 A.U. Since $\sin \theta$ cannot be greater than 1, first order Bragg reflections of neighboring planes of a set require that $\lambda$ should be 2 A.U. or less. Hence X-rays with wavelength less than 2 A.U. are most useful in studying crystals. The energy of an X-ray photon is related to its wavelength $\lambda$ by,

$$E = h\nu = \frac{hc}{\lambda}$$

X-rays emanating from 10 to 50 keV range are used.

Experimental methods in X-ray diffraction

1. Laue method
2. Rotating crystal method
3. Powder method

1. **Laue method**:

A single crystal is held stationary in a beam of continuous wavelength X-ray radiation. The crystal selects out and diffract the discrete values of $\lambda$ for which planes of spacing ‘$d$’ exist and incident angle ‘$\theta$’ satisfies the Bragg’s law.

2. **Rotating crystal method**:

Single crystal is rotated about the fixed axis in a beam of monochromatic X-rays. The variation in $\theta$ brings different atomic planes into position for reflection.
3. **Powder method**: A powdered sample of crystalline material is placed in a fixed position in a monochromatic beam among the distribution of the crystalline orientations there will be some for which the angle of incidence satisfies the Bragg’s law.

3.2.1 **Powder Diffractometer (XRD)**:

There are different types of X-ray diffractometers available for crystal structure analysis. It can also be used for nanomaterial’s analysis. The most commonly used diffractometer is known as Powder diffractometer or Debye-Scherer’s diffractometer after their inventors. This diffractometer is conceptually simple and allows quite an accurate determination of crystal structure of polycrystalline samples, thin films and nanoparticles.

It consists of a monochromatic source of X-rays (usually from a copper target or anode giving CuK$_\alpha$ radiation ($\lambda = 1.564056$ Å) after passing through nickel filter), sample holder and an X-ray detector. Both sample centre and normal to the plane of the paper. Samples in the form of powder, thin films etc. can be used. Sometimes sample heating / cooling facilities are provided.

The diffracted rays make angle 2\(\theta\) at the detector with respect to incident beam direction. A plot of intensity (counts), as a function of angle 2\(\theta\) (usually 20$^\circ$ to 160$^\circ$), is a diffraction pattern ready for analysis. Detector is a suitable photon counter like Geiger Mueller tube, proportional counter, scintillation counter etc. Usually, due to finite size of X-ray beam -1-2 mm$^2$, smaller angles (<20$^\circ$) are not accessible using these diffractometers. However for some detailed analysis of crystals or
nanoparticles, where additional information is needed at as small as $0 \sim 0.1^0 - 0.2^0$, modifications of Debye Scherrer Diffractometer or another diffractometer are needed.

### 3.2.2 APPLICATIONS OF XRD :-

- To identify crystalline phases and orientation
- To determine structural properties: Lattice parameters ($10^{-4} \text{ }^0 \text{ A}$), strain, grain size, epitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion.
- To measure thickness of thin films and multi-layers
- To determine atomic arrangement.

### 3.2.3 EXPERIMENTAL : To study crystal structure of Bismuth Iodate, Bismuth Iodide & Bismuth Trisulphide crystals by powder X-ray diffraction Method, X-ray diffraction was recorded on miniflex goniometer (Fig 3.2) at National Chemical Laboratory Pune, Pune 07

![FIG 3.2 miniflex goniometer](image_url)
3.3 FT-IR ANALYSIS OF GROWN CRYSTALS

FT-IR spectroscopy is one of the most powerful techniques which offers the possibility of chemical identification. This technique when coupled with intensity measurement may be used for quantitative analysis. FT-IR spectroscopy may be applied at all levels of expertise from a simple matching of spectra on one end to theoretical calculation at the other. The instrument is common, relatively inexpensive and easy to operate. The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of FT-IR radiation, the molecule of a chemical substance vibrate at many rates of vibration, giving rise to closely packed absorption bands called as FT-IR absorption spectrum, which may extend over a wide wavelength range. Various bands will be present in FT-IR spectrum, which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus, FT-IR spectrum of a chemical substance is a ‘finger print’ for its identification. Band position in FT-IR spectrum may be expressed conveniently by the wave number $\nu$ whose unit is cm$^{-1}$. The relation between wave number $\nu$ and wavelength $\lambda$ and frequency $\nu$ is as follows

$$\nu = \frac{c}{\lambda}$$

Where $c$ is the velocity of light. From the above relation it follows that; wave number is a reciprocal of wavelength.
Band intensity in FT-IR spectrum may be expressed either as transmittance (T) or absorbance (A). Transmittance is defined as the ratio of radiant power transmitted by a sample to the radiant power incident on the sample. On the other hand, absorbance is defined as the logarithm to the base 10 of the reciprocal of the transmittance i.e.

\[ A = \log_{10} \left( \frac{1}{T} \right) \]

3.3.1 The range of FT-IR Radiation:

The infrared radiation refers to that region of electromagnetic spectrum which lies between the visible and microwave regions. However, this region may be divided into four sections.

a. The photographic region – This ranges from visible to 1.2 µm.
b. The Very Near infrared region – This is also known as overtone region and ranges from 1.2 to 2.5 µm.
c. The Near Infrared region – This is also known as the vibration region and ranges from 2.5 to 25 µm.
d. The Far Infrared region – This is known as rotation region and ranges from 25 to 300-400 µm.

When an analytical chemist speaks of infrared spectroscopy, he usually means the ranges from 2.5 to 25 µm or 4000 to 400 wave numbers (waves per cm or cm\(^{-1}\)). This range gives him the important information about the vibrations of molecules and hence about the structure of molecules.

FT-IR is Fourier Transform Infrared Spectrophotometer. A FT-IR instrument gives the same information as a simple Infrared spectrophotometer, however the performance overweighs with respect
to spend, sensitivity and much smaller requirement of the sample. The new model 16 PC FT-IR spectrometer from the Perkin Elmer model 783 is controlled by Digital Equipment Corporation 316-SX personal computer running infrared data manager software, offering users an analytical grade instrument with a variable resolution up to 2 cm\(^{-1}\) and a frequency range 4000 to 450 cm\(^{-1}\).

The FT-IR spectrum of an organic compound reveals a good deal of information about the functional group present in an organic compound.

### 3.3.2 Application of infrared spectroscopy

**I) Functional group region** – (2.5 to 7.7 µm) or (4000 to 1300 cm\(^{-1}\))

The common functional group shows absorption band in this region. The bands that occur in this region are due to stretching vibration as -O – H, - N – H, C – H, S – H in the region 3700 to 2500 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>4000</th>
<th>2500</th>
<th>2000</th>
<th>1500</th>
<th>1250</th>
<th>900</th>
<th>625</th>
</tr>
</thead>
<tbody>
<tr>
<td>- N - H</td>
<td>C = N</td>
<td>C = O</td>
<td>Finger print</td>
<td>Aromatic</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>region</td>
<td>region</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- O - H</td>
<td>C = C</td>
<td>C = N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- C - H</td>
<td>C = C</td>
<td></td>
<td>(Bending vibrations)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The appearance of absorption band at 2500 to 2100 cm\(^{-1}\) shows the presence of C≡C or C≡N band and is known as triple bond region. The FT-IR absorption band at 1600 to 1500 cm\(^{-1}\) indicate the presence of aromatic
C=C stretching frequency while at 1680 to 1620 cm\(^{-1}\) is due to alkane, C=C stretching frequency. The important FT-IR absorption band at 1700 cm\(^{-1}\) clearly indicates the presence of carbonyl group C=O may be aldehyde or ketone. Thus, function group in the molecule can be identified from absorption band in FT-IR.

II) **Finger print region:** – (7.7 to 11 µ) or (1300 to 909 cm\(^{-1}\))

   It is very complex and is a characteristic for a specific module. This region is useful for sample comparison and is known as finger print region. This is the most complex part of FT-IR spectrum and contains number of absorption band. These absorption bands appear due to stretching and bending vibrations. This region is not of much use for interpretation but helpful for sample comparison. If the finger print region of two samples is identical, then these samples are also identical.

III) **Aromatic region:**

   The region between (11 - 15 µ) or (909 to 667 cm\(^{-1}\)) is known as Aromatic region. This part is useful for detection of aromatic character of the compound. The bands occur in this region are due to bending vibrations in the molecule. The lack of absorption in this region shows presence of non aromatic compound. This region also helps in determining aromatic substitution pattern such as ortho, Meta, Para substitution.

   Infrared spectroscopy can be used to identify material. It can determine the composition of the mixture, monitor the course and extent of reaction and provide information useful in reducing molecular
structure. Analysis by infrared spectroscopy is based on the fact that molecules have specific frequency of internal vibration. These frequencies occur in the infrared region of the electromagnetic spectrum 4000 cm\(^{-1}\) to 200 cm\(^{-1}\) by Kalsi [13]. When the sample is placed in the beam of infrared radiation, it will be absorb radiation at frequency corresponding to the molecular vibrational frequency and its amplitude changes will transmit all other frequencies. The frequencies of the radiation absorbed are measured by infrared spectrometer and the resulting plot of absorbed energy V/s frequency is called as infrared spectrum of the material. Identification of the substance is possible because different materials have different vibration and yield different infrared spectrum. Furthermore, from the frequencies of absorption it is possible to determine whether various chemical groups are present or absent in the given chemical structure. In addition to characteristics nature of the absorption, the magnitude of the absorption due to given species is related to the concentration of that species.

### 3.3.3 Molecular Vibrations:

There are two types of molecular vibrations, stretching and bending. Molecules have rigid bond lengths and bond angles.

![Symmetrical stretching](image.png)

**Fig 3.3 Indicate symmetrical stretching**
The symmetrical stretch of CO$_2$ is inactive in the FT-IR because this vibrations produces no change in the dipole moment of the molecule, in order to be active, a vibration must cause a change in the dipole moment of the molecule.

3.3.4 Stretching Vibrations:

The stretching frequency of a bond can be approximated by Hook’s law. In this approximation two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses joined by a spring.

Infrared spectroscopy has wide application in industries, especially in chemical factories. Infrared spectra give information about the presence of specific functional groups in the molecule. Each functional group absorbs specific frequency radiations. Due to which amplitude of vibrations is increased and thereby absorption band at different frequencies are recorded, nature of bonding and forces working between atoms can be predicated. Infrared spectra give information about the structural formula, the absence of the gel inclusion in the crystal and hence the identity of the crystal.

3.3.5 Bending:

In which the position of the atoms changes relative to the original bond axis. Bending vibrations generally requires less energy and occur at longer wavelength.
Band Intensities in FT-IR spectrum may be expressed as Transmittance (T) or Absorbance (A).

**Transmittance:**

It is defined as the ratio of radiant power transmitted by a sample Chatwal (1984) [14].

**3.3.6 Absorbance:**

It is defined as the algorithm to the base 10, of the reciprocal of the transmittance i.e. $A = \log_{10} \left( \frac{1}{T} \right)$. The applications of infrared spectroscopy have been expensively covered by Little (1967) [15], Hair (1967) [16].

Infrared spectroscopy has wide applications in industries, especially in chemical factories. Infrared spectra give information about the presence of specific functional group absorbs specific frequency radiations, due to which amplitude of vibrations is increased and there by absorption band at different frequencies are recorded. Therefore presence of functional groups, water molecules, nature of bonding and forces working between them atoms can be predicted. Infrared spectra gives information about the structural formula, Stanley (1987)[17], Morrison and Boyd (1989) [18], Jeffery (1989) [19], Silverstein (1991) [20].

The absence of gel inclusion in the crystal and hence the identity of the crystal. In the presence work, infrared spectra of Bismuth Iodate, Bismuth Iodide, and Bismuth Trisulphide were recorded using SHIMADZU spectrometer at dept. of chemistry in University of Pune, as shown in Fig 3.5.

**3.3.7 Experimental:**

For infrared analysis of the crystal, samples are prepared in the form of pallet by taking about 90-100 mg of the sample, mixed with 0.5
gm of analytical grade dry potassium bromide. The mixture is finely powdered and is taken in a die. The die is first evacuated to a pressure of $10^{-3}$ torr, and then subjected to extremely high pressure (about 1200 kg cm$^{-3}$) about five minutes. This process results into the formation of a fine palate, which is removed from the die and is used for scanning the spectrum. The FT-IR spectrum recorded for Bismuth Iodate, Bismuth Iodide and Bismuth Trisulphide crystals are shown at their respective chapters.

![Fig 3.5 Perkin-Elmer Spectrometer](image)

3.4 Thermal Analysis:-

The term “Thermal analysis” incorporates those techniques in which some physical parameter of the system is determined and or recorded as a function of temperature. The various techniques of thermal analysis are summarized in table 3.1.
### Table 3.1 Thermal Analysis Techniques

<table>
<thead>
<tr>
<th>Name of the Technique</th>
<th>Abbreviation of the Technique</th>
<th>Instrument Employed</th>
<th>Parameter Measured</th>
<th>Drawing of the Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Thermogravimetry</td>
<td>TG</td>
<td>Thermobalance</td>
<td>Mass</td>
<td>Mass vs Temp or Time</td>
</tr>
<tr>
<td>2. Derivative thermogravimetry</td>
<td>DTG</td>
<td>Thermobalance</td>
<td>dm/dt</td>
<td>dm/dt vs Temperature</td>
</tr>
<tr>
<td>3. Differential Thermal Analysis</td>
<td>DTA</td>
<td>DTA apparatus</td>
<td>∆T</td>
<td>∆T vs Temperature</td>
</tr>
<tr>
<td>4. Differential Scanning Calorimetry</td>
<td>DSC</td>
<td>Calorimeter</td>
<td>dh/dt</td>
<td>dh/dt vs Temperature</td>
</tr>
<tr>
<td>5. Thermometric Titrimetry</td>
<td>---</td>
<td>Calorimeter</td>
<td>Temperature</td>
<td>Temperature vs Titrant Volume</td>
</tr>
<tr>
<td>6. Dynamic Reflectance Spectroscopy</td>
<td>DRS</td>
<td>Spectrophotometer</td>
<td>Reflectance</td>
<td>% Reflectance and Temperature</td>
</tr>
<tr>
<td>7. Evolved Gas Detection</td>
<td>EGD</td>
<td>Thermal Conductivity</td>
<td>Thermal Conductivity (T.C)</td>
<td>T.C vs Temperature</td>
</tr>
<tr>
<td>8. Thermomechanical Analysis (Dilatometry)</td>
<td>TMA</td>
<td>Dilatometry</td>
<td>Volume vs Length</td>
<td>Volume or Length vs Temperature</td>
</tr>
<tr>
<td>9. Emanation Thermal Analysis</td>
<td>ETA</td>
<td>BTA apparatus</td>
<td>Radioactivity (E)</td>
<td>E vs Temperature</td>
</tr>
</tbody>
</table>

In this table, each technique is listed in terms of the parameter recorded and the instrumentation involved. It is not possible to discuss all the technique given in table. However, we shall discuss some of these techniques

- Thermo Gravimetric Analysis [TGA]
3.4.1 THERMOGRAVIMETRY [TGA]

Thermal Gravimetric Analysis is a simple analytical technique that measures the weight loss or weight gain of material as a function of temperature. As materials are heated they can lose weight from a sample by process such as drying, or from chemical reactions that liberate gases. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss or gain are disruptive process to the sample material or batch, knowledge of the magnitude and temperature range of those reaction are necessary in order to design adequate thermal ramps and holds during those critical reaction periods.

**TGA Principle and Operation**

Sample of the test material is placed into the high alumina cup that is supported on, or suspended from an analytical balance located inside the furnace chamber. The balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted into percentage weight change on the Y-axis against the reference material temperature on the X-axis.

**Temperature Ranges:** There are three temperatures ranges and four types of furnaces for those ranges.
1. Room temperature to $1200^\circ$ C Kanthal wire wound heating element.

2. Room temperature to $1600^\circ$ C platinum alloy wire wound heating element silicon carbide heating element.

3. Room temperature to $1700^\circ$ C molybdenum disilicide heating element.

**Heating Rates:**

Most ceramics samples are normally heated from ambient to the maximum temperature at $30^\circ$ C per minute. Slow heating rates are preferred so that the weight change can occur over a narrow time span and temperature range. The resulting curve is steeper and the onset temperature range is closer to the actual. Fast heating rates spread the weight change over wider time span and temperature range, and generate less steep curves and shift the onset temperature above the actual. Orton control systems provide the ability to set various heat up rates according to the user’s requirement.

**Thermal Cycle:**

Most TGA’s are performed at standard heating rate to the maximum temperature then discontinued. The thermal cycle can be extended to include the cooling data. Other programmed cycles that contain multiple ramps and soaks such as actual production drying or firing schedules are available.

**Atmospheres:**

For most ceramics materials, TGA test are normally performed in ambient air. The TG-730 and TG-740 set TGA’s are designed for ambient air or inert atmosphere operation. The TGA-720 series are used for other controlled atmospheres including vacuums.
3.4.2 DIFFERENTIAL THERMAL ANALYSIS [DTA]

DTA involves heating or cooling a test sample and an inert reference under identical conditions. While recording any temperature difference between the sample and reference. This differential temperature is then plotted against time, changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert references. A DTA curve is used as finger print for identification.

Interpretation and Presentation of data:

A simple DTA curve consist of linear portions displaced from the abscissa because the heat capacities and thermal conductivities of the test and reference samples are not identical, and of peaks corresponding to the evolution or absorption of heat following physical or chemical changes in the test sample. The peak area (A), which is related to enthalpy changes in the test sample that enclosed between the peak and the interpolated baseline. The area under a DTA peak can be to the enthalpy change and is not affected by the heat capacity of the sample. DTA may be defined formally as a technique for recording the difference in the temperature between a substance and a reference material against either time or temperature two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

In differential thermal analysis (DTA) the temperature of a sample and a thermally inert reference material are measured as a function of temperature (usually sample temperature). Any transition, which the sample undergoes, will result in liberation or absorption of energy by the
sample with a corresponding deviation of its temperature from that of the reference. The differential temperature ($\Delta T$) versus the programmed temperature ($T$) at which the whole system is being changed tells the analyst the temperature of transitions and whether the transition is exothermic or endothermic. TGA and DTA analytical methods incorporate those techniques in which some physical parameters are the function of temperature. Duval (1963)[21], Keattch (1969) [22]and Wendiandt (1974) [23], Skoog[24], Wiliam[25]and Chatval [26]have suggested various applications of the thermal analysis. TGA and DTA give information regarding the thermal stability of the compound.

3.4.3 DIFFERENTIAL THERMO GRAVIMETRY [DTG]

Thermogravimetry (TG) provides the analyst with a quantitative measurement of any weight change associated with a transition. For example, TG can directly record the loss in weight with time or temperature due to dehydration or decomposition. Thermogravimetric curve are characteristics for a given compound or systems because of the unique sequence of physio-chemical reactions, which occur over definite temperatures ranges and at rates that are a function of the molecular structure, changes in weight are a result of the rupture and /or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile product or the formation of heavier reactions products. From such curves data are obtained concerning the thermodynamics and kinetics of the various chemical reactions, reaction mechanism and the intermediate and final reaction products. The usual temperature range is from ambient to $1200^\circ$ C with inert or reactive atmospheres. The derivative in TG is often used to pinpoint completion of
weight loss steps or to increase resolution of overlapping weight-loss occurrences.

**Applications:** Some of the applications of Thermogravimetry are of particular importance to the analyst. These are:

- The determination of the purity and thermal stability of both primary and secondary standards.
- The investigation of correct drying temperatures and the suitability of various weighing forms for gravimetric analysis.
- Direct application to analytical problems (automatic Thermogravimetric analysis).
- The determination of the composition of complex mixtures.

In the present work, thermal analysis (TGA and DTA) of grown crystals was carried out using PerkinElmer Diamond TGA/DTA Instrument at National Chemical Laboratory, Pune. Its experimental setup are as shown in fig 3.6[a] and 3.6[b] respectively.

**3.4. 4 DIFFERENTIAL SCANNING CALORIMETRY [DSC]**

Closely related to DTA is differential scanning calorimetry (DSC). In this method the sample and reference material are also subjected to a closely controlled programmed temperature. In the event that a transition occurs in the sample, however, thermal energy is added to or subtracted from the sample or reference containers in order to maintain both sample and reference at the same temperature, because this energy input is precisely equivalent in magnitude to the energy absorbed or
evolved in the particular transition, a recording of this balancing energy yields a direct calorimetric measurement of the transition energy.

In addition to determination of heats and temperature of physical and chemical transitions, DSC is also useful to finding out calorimetric purity and second order transitions. In this technique aluminum pan is used to accommodate the weighted sample powder. The medium used air and is supplied at the rate of 100ml/min. The sample is heated at the rate of 5°C/min up to 600°C. Here change in energy say mW, is recorded as a function of temperature, which provides exothermic or endothermic peaks at the time of dehydration or decomposition reaction. Probably the common use of DSC curve is finger printing in which simple or complex materials can be compared for identification using measurement of peak positions, size or shape. In DSC the range of temperature for experimentation is 180 to 1000°C.

Fig 3.6.a PerkinElmer Diamond TGA/DTA   Fig 3.6.b
In the present work, DSC studies of grown crystals were carried out using Metlar TA 4000 Instrument at National Chemical Laboratory, Pune. Its experimental setup are as shown in fig 3.6[c] and 3.6[d] respectively.

3.5 Chemical Analysis:

In a modern industrial society, most manufacturing industries rely upon both qualitative and quantitative chemical analysis to ensure that the raw materials used meet certain specifications, they also check the quality of the products, for this purpose, analytical methods must be employed which are quick and can be readily adopted for routine work. For the quantitative analysis of the substance, gravimetry, titrimetry or volumetric methods are useful according to Vogel (1977)[27]. In gravimetric analysis the substance being determined is converted into an insoluble precipitate, which is collected and weighed. In titrimetric analysis the substance to be determined is allowed to react with an appropriate reagent added as a standard solution and the volume of solution needed for complete reaction is determined.
3.5.1 Gravimetric Analysis:

Gravimetric analysis or quantitative analysis by weight is the process of isolating and weighing an element or a definite compound of the element in as pure a form as possible. The element or compound is separated from weighed portion of the substance being examined. A large proportion of the determinations in gravimetric analysis are concerned with the transformation of the element or radical to be determined into a pure stable compound which can be readily converted into a form suitable for weighing. The weight of the element or radical may be then readily calculated from knowledge of the formula of the compound and the relative atomic masses of the constituent elements. The separation of the element or of the compound containing it may be effected in a number of ways, the most important of which are:

- Precipitation methods
- Volatilization or evolution methods
- Electro analytical methods
- Extraction and chromatographic methods

The advantages of gravimetric analysis are:
1. It is accurate and precise when using modern analytical balances.
2. Possible sources of error are readily checked, since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities.
3. It has the important advantage of being an absolute method i.e. one involving direct measurement without any form of calibration being required.
4. Determination can be carried out with relatively inexpensive apparatus, the most expensive requirements being a muffle furnace and in some cases platinum crucibles.

Two general application of gravimetric analysis are:

- The analysis of standards which are to be used for the testing and/or calibration of instrumental techniques.
- Analysis requiring high accuracy, although the time-consuming nature of gravimetry limits this application to small numbers of determinations.

3.5.2 Titrimetric Analysis:

The term “titrimetric analysis” refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined. The solution of accurately known strength is called the standard solution reported by Vogel [28] and supported by Gray [29], Sharpe Willam [30], Shriver [31], Puri [32], Cotton [33], and Lee [34]. The weight of the substance to be determined is calculated from the volume of the standard solution used and the chemical equation and relative molecular masses of the reacting compounds. The term ‘volumetric analysis’ was formerly used for this form of quantitative determination but it has been replaced by titrimetric analysis.

For titrimetric analysis conditions
1. There must be simple reaction which can be expressed by a chemical
equation; the substance to be determined should react completely with
the reagent in stoichiometric or equivalent proportions.

2. The reaction should be relatively fast (Most ionic reactions satisfy this
condition). In some cases the additions of catalyst may be necessary to
increase the speed of a reaction.

3. There must be an alternation in some physical or chemical property of
the solution at the equivalent point.

4. An indicator should be available which, by a change in physical
properties (colour or formation of a precipitate), should sharply define
the end points of the reaction. [If no visible indicator is available, the
detection of the equivalence point can often be achieved by following
the course of the titration by measuring

a. The potential between an indicator electrode and a reference
electrode (potentiometric titration).

b. The change in electrical conductivity of the solution (conductimetric
titration)

c. The current which passes through the titration cell between an
indicator electrode and a depolarized reference electrode at a suitable
applied e.m.f. (Amperometric titration).

d. The change in absorbance of the solution (spectrophotometric
titration).
Titrimetric methods are normally capable of high precision (1 part in 1000) and wherever applicable possess obvious advantages over gravimetric methods.

3.5.3 Specific Gravity:

Specific gravity may be defined as the ratio of mass of substance to the mass of an equal volume of other substance taken as a standard e.g. For Bismuth Iodate water may be standard.

In the present work, Chemical analysis of Bismuth Iodate, Bismuth Iodide & Bismuth Trisulphide crystals was carried out at Department of Chemistry, Smt. G. G. Khadse Science, Arts and Commerce Collage Muktainagar.

3.6 Energy Dispersive Analysis by X-Rays [EDAX]:

EDAX means Energy Dispersive Analysis. It is sometime referred as EDX or Elemental analysis. The percentage of cations and anions present in the crystal was estimated by EDAX. In the present work, Energy Dispersive Analysis by X-Rays, of grown crystals were carried out at National Chemical Laboratory, Pune on the Elements in an Electron spectrum is as shown in fig 3.7. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDAX analysis system works as an integrated feature of a scanning electron microscope [SEM], and cannot operate on its own without latter.
Fig: 3.7 Elements in an EDAX spectrum are identified based on the energy content of X-Ray emitted by their electrons as these electrons transfer from higher –energy shell to lower –energy shell.

During EDAX analysis the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electron collide with the specimen atoms own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher- energy electron from an outer shell. to be able to do so. However the transferring outer electron must give up some of its energy by emitting an X-Ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-Ray with unique amount of energy during the transferring process. Thus by measuring the amount of energy present in X-Ray being released by a specimen during electron beam bombardment, the identity of the atom from which the X-Ray was emitted can be established.
The output of an EDAX analysis is an EDAX spectrum. The EDAX spectrum is just a plot to how frequently an X-Ray is received for each energy level. An EDAX spectrum normally displays peaks corresponding to the energy levels for which the most X-Rays had been received. Each of these peaks are unique to an atom, and therefore correspond to a single element. The higher peak in a spectrum, the more concentrated the element is in the specimen.

The EDAX spectrum plot only identifies the element corresponding to each of its peak, but the type of X-Ray to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by X-Ray emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-Ray emitted by M-shell electron going to the K-shell is identified as a K-Beta peak, as shown in figure 3.7. The principle underline EDAX is same as that of electron probes microanalysis. When a beam of electron strikes a specimen, a fraction of incident electron exits the atoms of the specimen, which then emit X-Rays when they return to their ground state. The energy of these X-Rays is strictly related to the atomic number of the elements exited and therefore their detection from the basis of elemental analysis in electron microscope.

A lithium drifted silicon P-I-N diode held at liquid nitrogen temperature is used as the detector of the X-Rays generated. A beryllium window covers the cooled detector. The output pulses are stored in multichannel analyzer. The analysis of spectrum is carried out by energy dispersion method. This method can detect elements from sodium upwards in the periodic table. The quantitative electron limit for
homogeneously distributed elements is often 0.1-0.01 atomic percentage.

3.7 Electron Microscopy:

In electron microscope extremely short wavelength electron beam is used. It therefore provides very high magnification and high resolution. It uses magnetic lenses and magnetic field to provide the image. Electron microscope is of two types.

I. Transmission electron microscope.

II. Scanning electron microscope.

I. Transmission Electron Microscope (TEM).

In TEM, the specimen to be examined is prepared as an extremely thin film. The electron beams arises from tungsten filament and passes through the specimen. The magnetic coils are used to magnify the image and final enlarged image can be viewed on fluorescent screen or photographic plates. It gives magnification of about 5, 00,000 to 10, 00,000 times.

II. Scanning Electron Microscope (SEM).

In SEM, the specimen is not very thin specimen but beam impinge on its surface from above. The specimen may be opaque and may be of any manageable thickness and size. The specimen is subjected to a narrow electron beam which rapidly moves over the specimen. This causes release of secondary electrons and other types of radiations from the specimen surface. These electrons are collected by a detector which generates an electrical signal. These signals are then scanned in the
manner of a TV system to produce an image on a cathode ray tube. SEM gives about 10,000 to 1,00,000 times magnification.

<table>
<thead>
<tr>
<th>Type of microscope</th>
<th>Maximum useful magnification</th>
<th>Resolution (nm)</th>
<th>Common uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>10000 to 100000</td>
<td>1 to 10</td>
<td>Used for observing detailed surface structure of microorganisms as it produces three-dimensional topographic image</td>
</tr>
</tbody>
</table>

**Principle:**

In scanning electron microscope electrons are not transmitted though very thin specimen but impinges on its surface. A narrow beam of electron with high velocity originate from electron gun, passes through condenser lens and other magnetic lens, they produce and focus electron beam to 5-10 nm diameter into a spot on specimen surface. The electron probe move rapidly back and forth (raster pattern). The electron probe while scanning the specimen surface, excite specimen molecule to high energy level. Such energy is released by exited molecule in several forms including high energy electron (secondary electron). The number of secondary electrons released depends on three dimensional shape of specimen surface. These secondary electrons are deflected towards collector-detector and are converted into pulses of electric current. These successive electric signals are amplified and transmitted to cathode ray tube for production of image on TV screen. CRT beam and scanning beam are synchronized which help to see image of object on TV screen. Upadhaya A and Upadhaya K [35], Wilson [36], Aneja [37], Rastogi [38] and Narayanan [39], describe the formation of these images in detail.
Working:-

The electrons are originated through tungsten or lithium hexaboride gun. This electron beam is broad, hence it is sharply focused, adjusted and demagnified by arrangement of magnetic lens which are functionally similar to condenser of light microscope. Thus electron beam is made needle sharp. The diameter of such probe is 5 to 10 nm. It scans the specimen by raster pattern. The electron probe enters to great depth and resolves the details up to 20 nm. The movement of electron beam is facilitated by beam deflector. The beam deflector is charged plate which attracts or repels electron beam. It is placed below demagnifying lens system. When the electron beam strike on object, it generates secondary electrons as described in principle. The secondary electrons are detected, collected and converted in to electric current. Such low electron pulses are amplified by video amplifier and amplified signals are supplied to CRT. Scanning probe and CRT are synchronized so that image seen is really a picture of different point in continuous fashion.

Application of Electron Microscopy:-

- Studies in crystallography, magnetic and electrical carrying specimens.
- SEM used in study of properties of gel, smoke.
- SEM used to reveal the surface details of specimen
- SEM helps in investigation of forensic science.
- Structural study of various cell parts such as cell wall, cell membrane, flagella, cell organelles etc.
- In Biology. Medicinal effect on various organs such as kidney is performed by electron microscope.
• Chromosomal organization can be studied using electron microscope.
• Study of virus structure and assembly.

In the present work, Scanning Electron Microscope of grown crystals was carried out at National Chemical Laboratory, Pune on the Scanning Electron Microscope, is as shown in fig 3.8.

![Image of Scanning Electron Microscope]

**Fig: 3.8 Scanning Electron Microscope.**

**3.8 Magnetic Susceptibility (χ) :**

Magnetic Susceptibility is defined as the ratio of the intensity of magnetization (I) to the strength (H) of the magnetizing field.

\[ \chi = \frac{I}{H} \]

Diamagnetic bodies have a negative Susceptibility, while paramagnetic bodies have a positive Susceptibility as defined by Dutta [40] and Nigvekar [41].
There are three methods for measurement of Susceptibility.

1. Farady method.
2. Gouy method.
3. NMR method.

In the present work Gouy’s method was used for the Susceptibility measurements. The experiments were carried out at Department of Physical science N.M.U Jalgaon. The experimental setup is shown in fig 3.9

![Experimental setup for Magnetic Susceptibility](image)

**Fig: 3.9 Experimental set up for Magnetic Susceptibility**

In this method, a sample was used in the powder form and put in the sample holder which was suspended with a thread of non magnetic material between the pole pieces of the magnet. The other end of thread was connected to the one pan balance kept in a magnetic field free space and from observations, Magnetic Susceptibility \( (\chi_g) \) were calculated which are discussed in chapter no 4, 5, 6 for Bismuth Iodate, Bismuth Iodide and Bismuth Trisulphide respectively.
The magnetic susceptibility of the material is the measure of the capability of the material to take up magnetization. In many materials the magnetic moment per unit volume i.e. magnetization $M$ is directly proportional to the applied magnetic field $H$.

In such case $\overline{M} = \chi \overline{H}$

Hence, constant of proportionality is called magnetic susceptibility $\chi$ which is unit less.

### 3.8.1 Classification of magnetic materials:

Magnetic materials are capable of being magnetized in a magnetic field, i.e. of creating their own magnetic field. According to their magnetic properties, such materials are classified into following groups,

- Paramagnetic Materials.
- Diamagnetic Materials.
- Ferromagnetic Materials.
- Antiferromagnetic Materials

#### 3.8.8.1 Paramagnetic Materials:

When some materials placed in an external magnetic field get slightly magnetized in the direction same as that of external field are known as paramagnetic materials and the magnetism possessed by them is called paramagnetism. Some examples of paramagnetic materials are Aluminum (Al), Platinum (Pt), Sodium (Na), Copper chloride (CaCl₂), Oxygen (O₂), solutions of salts of Fe and Ni etc.
Characteristics of paramagnetic materials:

- Magnetic susceptibility ($\chi$) of these materials varies inversely as the absolute temperature. It decreases with rise in temperature. At some high temperature $\chi$ becomes negative and the substance exhibits diamagnetic properties.
- If a paramagnetic material is placed in a non-uniform magnetic field, it is attracted towards the regions of the stronger magnetic field. If a paramagnetic liquid is placed in a watch glass resting on the poles of a powerful electromagnet, the liquid is found to rise up at the points of greatest magnetic field.
- These materials have small positive value of magnetic susceptibility ($\chi$) ranging from $10^{-6}$ to $10^{-3}$ and the relative permeability ($\mu_r$) slightly larger than unity.
- When a rod of paramagnetic material is suspended freely in uniform external magnetic field, it rotates until its longest axis become parallel to the direction of the field.

3.8.1.2 Diamagnetic Materials:

When some materials placed in a strong external magnetic field get slightly magnetized in the direction opposite to that of external field are known as diamagnetic materials and the magnetism possessed by them is called diamagnetism. Some examples of diamagnetic materials are Bismuth (Bi), Copper (Cu), Zinc (Zn), Silver (Ag), Gold (Au), Diamond (C), Mercury (Ag), NaCl, Water (H$_2$O), Nitrogen (N$_2$), Hydrogen (H$_2$) etc.
Characteristics of diamagnetic materials:

- The Magnetic susceptibility of diamagnetic material is found to be independent of temperature (except Bismuth).
- If a diamagnetic material is placed in a non-uniform magnetic field, then it tends to move from stronger to weaker region of the magnetic field. If a diamagnetic liquid is placed in a watch glass resting on the poles of a powerful electromagnet, the liquid is found to accumulate on the sides where the field is weaker and gets depressed in the middle where the field is stronger.
- These materials have negative value of magnetic susceptibility ($\chi$) ranging from $10^{-9}$ to $10^{0}$ and the relative permeability ($\mu_r$) is always less than unity.
- When a rod of diamagnetic material is suspended freely in uniform external magnetic field, it rotates until its longest axis become perpendicular to the direction of the field.

3.8.1.3 Ferromagnetic Materials:

When some materials placed in an external magnetic field get strongly magnetized in the direction of the external fields are known as Ferromagnetic materials and the magnetism possessed by them is called as ferromagnetism. Some examples of Ferromagnetic materials are Iron (Fe), Nickel (Ni), Cobalt (Co), Gadolinium, Dysprosium etc.
Characteristics of Ferromagnetic materials:

- The magnetic susceptibility decreases steadily with rise in temperature according to Curie’s law $\chi \propto 1/T$ where $T$ is absolute temperature. Above a certain temperature called Curie temperature, the ferromagnetic materials become paramagnetic. For iron the Curie temperature is $770^0\text{C}$.

- Susceptibility remains constant for very small values of magnetic field increases for larger values and then decreases for very large values of magnetic field.

- These materials have large positive value of magnetic susceptibility and the relative permeability is also large of the order of hundreds and thousands. They are strongly magnetized by even a weak magnetic field.

- The intensity of magnetization is proportional to the magnetic field for smaller values of magnetic field, increases rapidly for larger values and attains a constant value for very large values of magnetic field.

- The magnetic induction varies with magnetic field in similar manner magnetization does, except the magnetic induction does not attain a constant value for very large values of magnetic field.

- Permeability also varies as magnetic susceptibility except at very high magnetic fields where Permeability decreases slowly in comparison to magnetic susceptibility.

- Ferromagnetic materials respond mechanically in an external magnetic field, changing their length slightly in the direction of the applied field. This property is called as magnetostriction.
3.8.1.4 Antiferromagnetic Materials:

Some materials just like ferromagnetic materials also have strong coupling forces between the atomic magnetic dipole moments, but their coupling forces produces antiparallel alignments of electron spins. The spins alternate in direction from atom to atom and results no net magnetic moment. This property is called as antiferromagnetic and the material possessing this property is known as antiferromagnetic materials. Some examples of antiferromagnetic materials are Chromium (Cr), Manganese (Mn), Hematite Fe₃O₄, MnF₂, Cr₂O₃ etc. When a ferromagnetic material is placed in an external magnetic field, a small magnetization appears in the direction of the field which increases further with temperature. The magnetization becomes maximum at a critical temperature called as Neel temperature, which is analogous to the Curie temperature in paramagnetic or ferromagnetic materials. Above this temperature, the spin directions are random.

3.9 ELECTRICAL CONDUCTIVITY

According to H. V. Keer [42] and Azaroff [43] the Electrical conductivity of material is the basic physical parameters and is affected by a number of factors such as impurities, vacancies and interstitials and also on variation of temperature and pressure. Most of the ionic crystals are insulators (i.e. bad electrical conductors) they exhibit conductivity at elevated temperature which is much lower than of metals. Again the measurement of conductivity for a single crystal can give useful information about the order in lattice. In the present investigation well known four probe method have been used, for the measurement of
electrical conductivity of Bismuth Iodate, Bismuth Iodide & Bismuth Trisulphide. The experiments were carried out at the Department of Chemical science, N.M.U, Jalgaon. The experimental set up and the schematic circuit diagram is as shown in fig 3.10.

Circular pallets of about 0.513cm height and 0.925 cm diameter were prepared from the powder of grown sample. (Bismuth Iodate, Bismuth Iodide & Bismuth Trisulphide) Then one of this pallet was fitted in the four probes of the sample holder which was then places in the furnace. The sample was heated in the furnace up to suitable temperature. The temperatures were recorded by using thermometer. The observations were recorded by passing constant voltage and the current was recorded for various temperatures from room temperature to $150^0$ C and electrical conductivity was calculated. The conductivity of ionic crystal is closely related to the chemical nature of the compound. They exhibit conductivity at elevated temperature which is much lower than that of metals. Moreover the conductivity of ionic crystal increases with increasing temperature in contrast with metals. These facts indicate that the charge carriers in ionic crystals are different from those in metals. Some conduction does occur by electron flow, but the electrons are so tightly bound in filled shells of the two types of ions (cations and anions) that they cannot move appreciably in an external electric field. Hence the charge transport is by charged ions themselves.

The electrical conductivity of a crystal alone was also measured. The ohmic contacts are made by applying silver paste on the surface of the crystal. Then it was observed that crystal conducts at lower temperature (at about $405^0$ k) compared to the pallet on the same.
Fig: 3.10 Electrical conductivity by four probe method

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