Chapter-2: Experimental Techniques

2.1 Introduction

Material synthesis and characterization are set to benefit from advances in the crystal growth technology. Advances in semiconductor research have major implications for the society. Therefore, innovation is necessary to drive growth methods and provide new inputs to improve quality of life. Practical testing of materials has evolved rapidly over the last decade. A description of the instrumentation and the operating procedure of the growth and characterization techniques used in the current study are provided in this chapter. For the right consistency and properties of the grown crystals, it is important to perform the different characterizations.

2.2 Preparation of Stoichiometric Charge:

Scientists face a considerable challenge in growing crystals of good quality with the desired stoichiometry and properties. The design of ampoules, synthesis of homogenous charges, and preparation of crystals are some of the approaches that require special attention. Selecting the right material for an ampoule should be the first step. For the purpose of avoiding contamination and reaction, select ampoule which has melting point higher than that of the compound. Thermal stress can be minimized by having a small expansion coefficient of the ampoule compared to its melting point [1]. The ease of sealing also contributes to flexibility in designing to the required shape.

Properties of the growing crystal are significantly affected by undesirable elements attached to the walls of the ampoule. Multiple nucleation and attachment of foreign atoms in ampoules may be enhanced if there are inorganic impurities. Cleaning the ampoules with hot water and soap solution in order to remove grease and dust. Dilute sulphuric acid and detergent were used to remove metallic pollutants from the surface. We have used ultrasonic cleaning with distilled water and then dried with air blow. Using a semi-microbalance (Fig.2.1), high purity chemical components (99.999%) bought from Sigma-Aldrich in India and the Nuclear Fuel Complex in Hyderabad were precisely weighed up to 10 micrograms before being put into a cleaned quartz ampoule with an internal diameter of 10 mm and a length of 100 mm. The material was sealed in the ampoule under vacuum pressure of 10^{-5} Pa (Fig. 2.2). A melt-stirring procedure was employed to create a homogenous mixture from the weighted quantities of the alloy's constituent parts. It is made up of a cylindrical resistance furnace with a core that is roughly 45 cm long and 5 cm in diameter. A ceramic tube that was 1.5 cm in diameter and 60 cm long was inserted into the cylindrical core. Inside this tube, a uniform temperature zone measuring between 10 and 12 cm in length was achieved. The tube's two ends were inserted into two brass sockets. To provide smooth travel without wobbling, the sockets were pivoted on frictionless bearings. An electrical motor rotated the tube at 10 revolutions per minute. In Fig. 2.3, a picture of the mixing unit is shown. For melting and stirring the charge, the vacuum-sealed quartz ampoule with the ingot was placed within the ceramic tube. About 50 ^{0}C above the material's melting point, the furnace core's maximum temperature was maintained. A proportional temperature controller was used to measure the temperature and regulate it (to within ± 5 ^{0}C). A Chromel-Alumel thermocouple was used to measure the temperature. The molten charge is stirred by the spinning and shaking of the quartz tube. This treatment was carried out for further two to three days to ensure thorough mixing and reaction of the charge. Afterward, the molten charge was gradually brought down to ambient temperature.

Figure 2.1: Weighing Balance

Figure 2.2: Vacuum Sealing Unit

Figure 2.3: Alloy mixing furnace

2.3 Crystal growth:

The method of crystallizing an alloy from its melt is highly important since it entails the transformation of atoms and molecules directly from liquid to solid and their systematic assembly into the crystalline structure from random distribution in the liquid state. Impurities can be reduced by taking special precautions during the crystallization process. Furthermore, the crystal can be doped with a specific impurity whose concentration is controlled. Several materials can form crystals from melt, including metals, alloys, semiconductors, superconductors and alkali halides.

During the growth process of crystals from melt, control must be maintained so as to advance one nucleus along with minimizing chemical and structural disorder in the crystal. By preventing extensive super-cooling zones in the melt, it is possible to prevent formation of new nuclei and instability of the crystal surface.

2.4 Zone melting Technique:

One of the best methods for growing single crystals of metal or alloy is the zone melting process (figure 2.4). The ingot is inserted into a long quartz tube using this technique. The diameter of the ingot was from 0.8 to 1 cm, and its length was roughly 6 cm. This technique involves creating a small molten zone that moves from one end of a huge solid ingot of the material to be crystallized to the other. Impurities are redistributed along the charge as the zone moves. After ten alternative zone passes, we obtained a single crystal that self-nucleated. We were able to obtain single crystals of high grade by giving the initial molten zone the requisite amount of time before beginning the zone trip. In this approach, growth velocity is crucial. The growth rate was 1 cm per hour. The same growth rate and temperature gradient were used to produce crystals with an x value as high as 0.2. By keeping the furnace temperature within +1 ºC, which results I n a zone length of about 1-2 cm, it was possible to achieve a temperature gradient across the two solid-liquid interfaces of about 650℃/cm. It was found that giving the first molten zone enough time before beginning the zone travel to achieve stable conditions was important to obtain crystals of high grade [2]. By looking at the cleavage surfaces, the quality of the crystals formed was assessed.

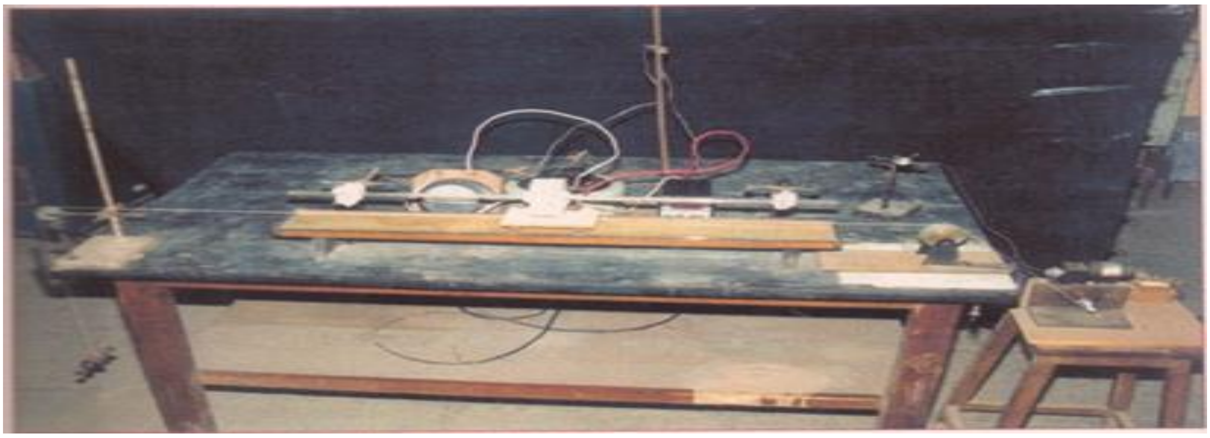

Figure 2.4: Zone Melting Unit

2.5 Scanning Electron Microscope:

Scanning electron microscope (SEM) is based on the principle of dual wave particle nature of radiations to acquire data regarding microstructure of crystalline materials. It is an established non-destructive tool used for imaging surface features with higher magnification, resolving power and field depth than an optical microscope. An e-beam produced from electron gun is focused on to the sample with a series of magnetic lenses and scattered electrons are captured by an analyzer to form the image [3].

2.6 Energy Dispersive Analysis by x-rays:

X-ray energy dispersive analysis, or EDAX, serves a variety of purposes in the field of industrial production, forensic investigation and academics. With EDAX mapping, spatial distribution of elements can be viewed qualitatively as well as quantitatively. Due to sample beam interaction, the atomic structure of each element determines the characteristic peaks on a spectrum produced by EDAX [4]. The EDAX technologies are based on the idea of elemental X-ray generation. On the specimen surface under inspection, an electron beam is applied. As a function of energy, the distinctive rays produced are examined, and the information gathered for the particular specimen helps in understanding the elemental percentage in the composition. Due to the usage of the electron beam as the source, EDAX and SEM are typically available in a single setup (Fig. 2.5). Chapter 3 discusses the elemental mapping and EDAX data for the grown $InBi_{1-x}Te_x$ (x = 0, 0.05, 0.1, and 0.15 crystals). The EDAX is usually available with the Scanning Electron Microscope (SEM).

Figure 2.5: Scanning Electron Microscope and EDAX System Setup

2.7 X-Ray diffraction techniques:

Whether a certain crystalline substance is present in its pure form or as one component of a mixture of other substances, it always results in a particular x-ray diffraction pattern. The use of the diffraction method for chemical analysis is based on this fact. For a qualitative investigation of the structure, samples in the form of aggregates of fine powder material or loose powders are characterized using the powder X-ray powder diffraction (XRD) technique. Because the intensity of the diffraction lines caused by one phase of a mixture depend on the amount of that phase in the material, quantitative analysis is also possible. Because it always differentiates between phases with the same chemical composition but distinct crystal structures, the powder technique is best known for its usage as a phase characterization tool. The diffraction method has so been extensively used for materials analysis. The powder sample is positioned in a collimated monochromatic X-ray beam when using the XRPD method. For the Debye-Scherrer camera technique, the sample may need to be crushed to fit within a glass capillary tube, rolled into a very thin rod shape, spread out thinly on a sample holder, or packed into a sample holder of a specific size. In certain cases, the preparation would be based on the instruments that are available and the type of testing. Digital or analogue techniques can be used to capture a diffraction pattern on photographic film. The final data can be shown as either a graph of intensity as a function of diffraction angle or intensity as a function of interplanar distance. Using search/match software and other computer tools, many modern automated powder diffractometers can provide further data reduction, including peak discovery and a tabular listing of peak an intensity vs interplanar spacing. Phase identification using XRPD is based on the unique pattern produced by every crystalline phase. All of these methods make use of the database maintained by the JCPDS international center of diffraction DATA [5]

Figure 2.6 shows the powder X-ray diffraction method's experimental setup. The following can be attributed to a system's primary function: A is an X-ray source that can be filtered to become monochromatic. The X-ray beam strikes the powdered material P after travelling through the slits S1 and S2. The slits' primary purpose is to narrow the X-ray beam. The X-rays exit the camera after striking the powder in order to reduce fogging brought on by direct beam scattering. As the powder sample and detectors are rotated, the intensity of the reflected X-rays is measured. The sample meets the Bragg's criteria for constructive interference when X-rays are incident on it, and a peak in intensity occurs. This X-ray signal is captured, analysed, and converted to a count rate by a detector before being sent to a device like a printer or computer monitor. Additionally, utilising the powder X-ray diffraction technique [9], one may do a mathematical analysis of the relative orientation of individual crystals within an aggregate. BRUKER AXS 08 Advance model X-ray diffractometer with CuKα_1 (= 1.54056 Å) radiation in the 2θ range of 10 to 80° was used to record the powder pattern with a scanning speed of 1 ° / minute for the sample. All the tests were conducted at room temperature with air as ambient.

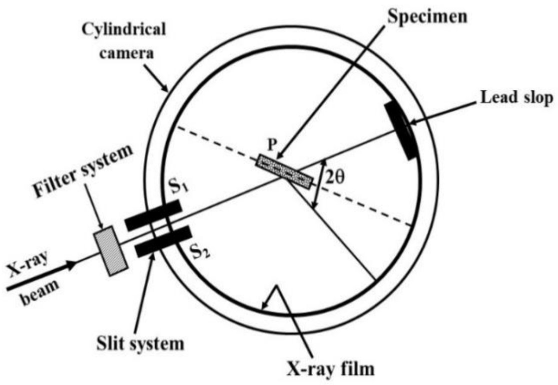

Figure 2.6: Experimental arrangement of a typical Powder XRD set-up

2.8 Pelletizer unit:

We have made pallets for FTIR characterization investigations at pressures up to 30 mbar using KBr. This unit is working on the oil pressure system (Fig.2.7). It has also provided a set of dies for this purpose.

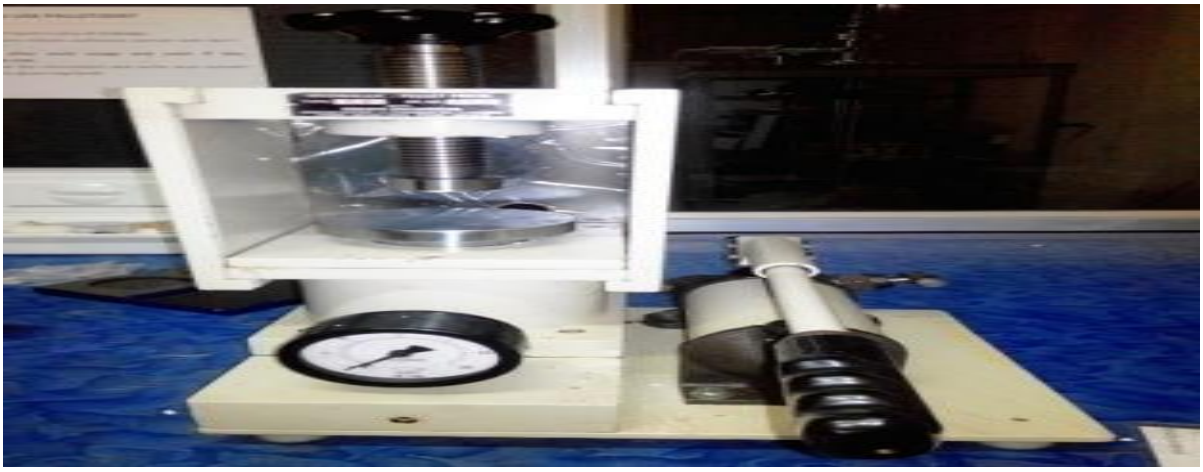

Figure 2.7: Pelletizer Unit

2.9 Fourier Transform Infrared (FT-IR) Spectroscopy:

FTIR spectroscopy is the most common method for detecting atom vibrations in molecules and crystals. The absorption spectrum highlights a molecule's functional groups and overall atom structure due to the multiplicity of vibrations evolving at the same time.

Functional groups in a sample can be assigned by comparing the acquired spectrum to the typical functional group frequency.

Chemical bonds in complex compounds are described by a distinctive characteristic absorption band that corresponds to the functional group. The stretching and bending modes of molecular vibration make up the majority of the spectrum. When infrared radiation strikes the molecules of the sample material, the molecules experience vibrational transitions, resulting in a shift in the dipole moment of the molecules. The resultant resonance absorption band appears at a certain frequency. Infrared section in the electromagnetic spectrum extends from the visible red end to the microwave region. Infrared (IR) radiations are produced by molecular vibrations such as rotating, stretching, bending, twisting, and so on. When IR radiation strikes a molecule, a certain percentage of the incident energy is absorbed at a given wavelength. Various vibrational transitions of molecules occur as a result of such absorption, resulting in a very complicated absorption spectrum. For the Mid IR (4000-400 cm^{-1}) area, FTIR is useful. The transmittance (T percent) or absorbance (A percent) of the vibrational band can be used to express the amplitude of the vibrational band as a function of wave number (cm-1). Figure 2.8 demonstrates how the Michelson Interferometer, on which the FTIR spectrometer is based, is integrated into the FTIR apparatus.

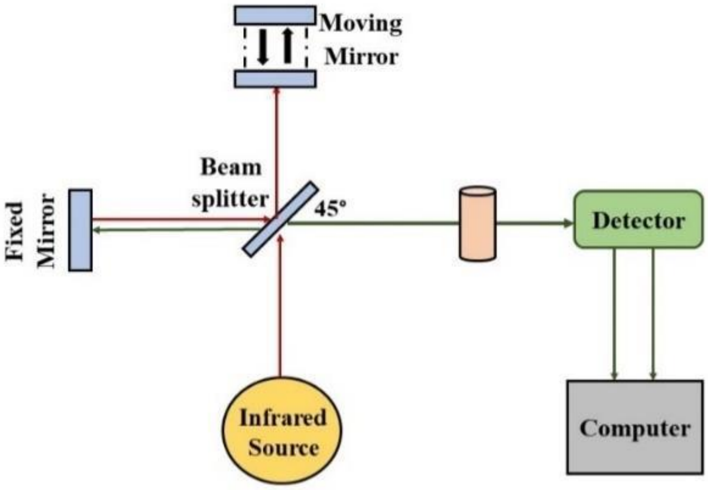

Figure 2.8: FTIR spectrometer photograph

Working of FTIR spectrometer:

Figure 2.8 above shows the FT-IR spectrometer's schematic diagram. The three primary parts of an FT-IR spectrometer are **1**. Drive mechanism **2.** Beam splitter **3.** Sources and transducers. The mirror collimates the IR light that the IR source emits. The beam splitter then separates the resulting beam. The beam splitter's fixed mirror receives half of the beam, while the moving mirror receives the other half. The mirrors have been placed to be at a right angle to each other. Depending on the path difference between the two reflected beams, interference occurs, either constructively or destructively. As the moving mirror shifts with constant velocity, the intensity of the emerging radiation is regulated sinusoidally. The detector can detect the signal of the sample now that the modulated signal has passed through it at the detector. A mathematical algorithm will be executed on the signal via computer software connected to the device, and the transmittance or absorption will be plotted against the wave number spectrum. The optical transmittance or absorption of the materials was measured using the I.R. Spectrophotometer [6] (FTIR, Japan, Jasco, 4100) [Fig.2.9] in the 400 cm^{-1} to 4000 cm^{-1} wave number range.

Figure 2.9: FTIR Spectrophotometer

2.10 Thermoelectric power Measurement:

A "Differential Temperature controller" (Scientific solution, Bombay) was employed to measure the Seeback coefficient as a function of temperature. In fig. 2.10, the thermoelectric power measurement system is displayed. The system is an integrated, flexible, and precisely designed setup for measuring the generated thermal E.M.F.

Figure 2.10: Thermoelectric power measurement set up

The sample holder is made up of two low power heaters A and B (15 Watt each). The temperature T of the heater A is measured by thermocouple (TC_1) and the temperature gradient ΔT between A and B is measured by differential temperature sensor (TC_2). The sample under investigation is placed directly on the heaters and is held by two pick up probes, which are of copper. The Seeback voltage is also measured between the ends of the sample with these probes. The instrument provides choice of temperature gradient to be used. The sample and the electronic circuit have been incorporated into one unit. Use of low power heaters and electronic controllers makes the operation very systematic and Seebeck coefficient of the sample can be measured.

If the temperature difference ΔT between the two ends of a material is small, the Seeback coefficient of a material is defined as:

$$S=\Delta V/\Delta T$$

where ΔV is the thermoelectric voltage seen at the terminals.

2.11 Hall Effect Measurements:

Among the intermetallic compounds, there are a large number of semiconductors which has presented a great need for methods to measure resistivity more accurately and quickly. Various sample geometries of films are in use; such as clove geometry and linear four probe geometry as described by Van der pauw [7] and Goswami [8]. If in a metal or a semiconductor sample, a current I is passed in a transverse magnetic field B, potential difference is produced in the direction normal to both the current and magnetic field directions.

This effect is called “**Hall Effect**” in honour of E. H. Hall, the physicist who discovered it in 1879.

Hall measurements were performed using linear four-probe geometry. A magnetic field applied perpendicular to the current deflects the charges carrier contributing to the current. Both the Hall voltage and the field voltage can be measured as a result of this process. A powerful electromagnet that can generate a magnetic field on the order of 3 kilo gauss is used to hold the sample between its two poles (Figure 2.11). A stabilized DC power source, the sample, and a sensitive current meter are all connected in series. A digital micro voltmeter is connected between the other two connections. In both the cases absence and presence of a magnetic field, current and voltage are monitored.

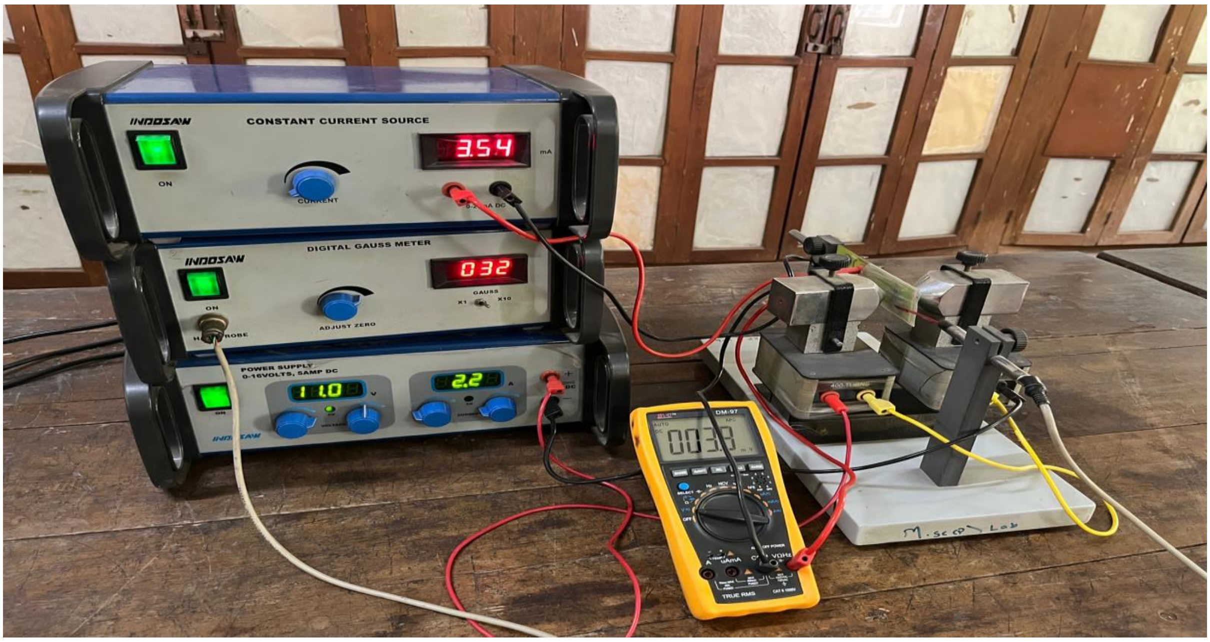

Figure 2.11: The Hall measurement set up

2.12 Micro Hardness Measurement Technique:

Vickers Microscope: The Vickers projection microscope was used to analyses the crystal surface on a micro photographic level. It is an optical microscope of the inverted metallurgical type. This microscope has two separate techniques for inspecting the crystals. In the current work, optically opaque crystals were used, and only the reflection mechanism was employed. Phase contrast and light profile techniques are also available with this equipment.

Measurement techniques:

Hardness can be measured by various methods:

1. Scratch method
2. Abrasive method
3. Plowing method
4. Rebound method
5. Damping method
6. Cutting method
7. Erosion method and
8. Static indentation method

The simplest and popular method among all of above is Static Indentations method.

VICKERS DIAMOND INDENTER:

The Vickers diamond indenter has a square base and a pyramidal shape with a semi-apex angle of 68º. By making indentation marks on the cleaved surfaces of the specimens under known applied loads, loading time, temperature, etc. the microhardness of the formed single crystals were studied. Its primary characteristic is that the impressions produced are geometrically symmetric. The Vickers hardness, $H_{v,}$ was calculated using the formula,

$$\mathrm{Hv} = \frac{1854 \times \mathrm{P}}{\mathrm{d}^2} \times \frac{9.8\ \mathrm{MPa}}{1} \text{ ---- } (2.1)$$

in accordance with the definition given by Cooke, Toughton [9], where P is load in gram and d is the average diagonal length of indentation mark in microns. To measure the diagonal of the indentation mark, a micrometer eye piece with the least count 0.19 micron (supplied with the tester) was used. The Vickers Microhardness Tester (supplied by M/s. Cooke Toughton and Simms Ltd., England) [10] was used with the Vickers projection microscope Fig 2.12. All of the supplier's guidelines were strictly followed.

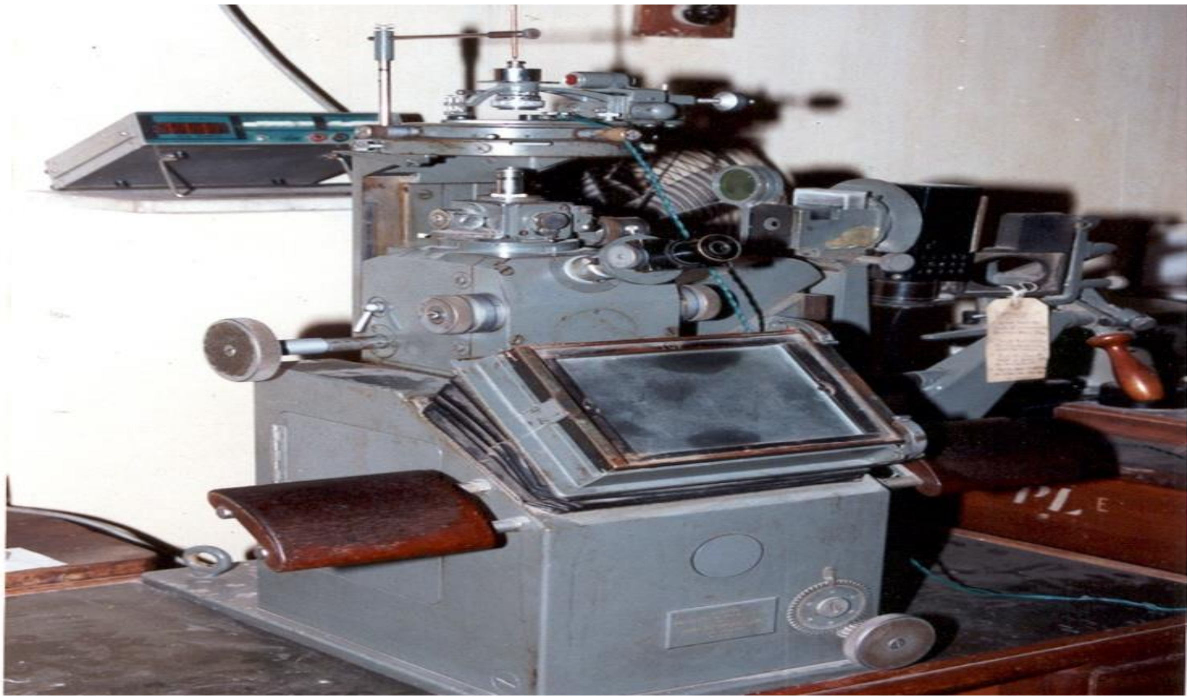

Figure 2.12: Micro hardness testing unit with the microscope

References:

[1] Shetty R., Wilcox W. R. and Regel L. L. Journal of Crystal Growth, Vol. 153, No. 2, (1995) 103.

[2] Ueda R. and Mullin J. B.: Crystal growth and Characterization North-Holland publishing company, New York (1975).

[3] Rita John., "Solid State Physics, e-book and reviews", McGraw-Hill Education, India, (2014).

[4] "Microscopy EKB Series", John Wiley & Sons, West Sussex (2015).

[5] Joint Committee on Powder Diffraction Standards (JCPDS), International Centre for Diffraction Data, Swarthmore, PA.

[6] Instruction Manual, FT/IR 4100, JASCO, Japan.

[7] Van der Pauw. L. J, Philips Res. Repto.13(1958) 1.

[8] Goswami. A and Ojna S.M, Thin solid films 16(1973) 187.

[9] Cooke Toughton and Simms, Photomicrography, 146 (1956) NY

[10] Cooke Toughton and Simms, Photomicrography, NY (England), 146(1996).