CHAPTER - 2

TECHNIQUES AND GRAPHICAL ANALYSIS

2.1 INTRODUCTION:

The various experimental techniques employed and graphical analysis carried out during the present investigation are briefly described in this chapter. For the quantitative and qualitative study of features on crystal surfaces, optical techniques were used. To study plastic deformation and other related phenomena the static indentation technique was employed. The diamond pyramidal knoop indenter was used with VERTIVAL incident light microscope. The crystals of sodium chloride, potassium chloride and potassium bromide were grown from melt.

The technique mentioned in this chapter are well discussed in several standard text books /1-6/. Hence only a brief description together with their salient features will be given here.

2.2 VERTIVAL INCIDENT LIGHT MICROSCOPE (CZ):

The VERTIVAL incident light microscope manufactured by Carl Zeiss (CZ), Jena is one of the best and sophisticated instruments amongst the metallurgical microscopes. It can be used for different types of illuminations. Its utility is enhanced by providing different attachments which can be fitted to this microscope, such as hardness testing unit, polarising accessories, multiple beam interference accessories, etc. For efficient use of

this instrument, it is imperative to be familiar with various parts, arrangements for adjustment of coarse motion brake and illuminating unit incorporating bright field and dark field, for the coordination of concave mirror condensers, etc. The instruction manual supplied by the manufacturer gives excellent account of this microscope and accessories. The basic unit of microscope consists of (i) the illuminating system, (ii) the stage for placing the sample, (iii) the body of the microscope carrying the objective and (iv) the monotube or binocular tube arrangement (Fig. 2.1). The ray diagrams for bright and dark field illuminations are shown in figures 2.2 and 2.3 . The focussing arrangement consists of fine focussing and coarse one. It is necessary to adjust the coarse motion brake.

(a) Adjustment of the coarse motion brake (Fig. 2.1) :

The instrument is supplied with the coarse motion brake released; hence the smoothness of the coarse motion mechanism has to be adjusted by the user. This is done by holding fast one pinion head [1] (Fig. 2.1) and moving the other in a clockwise direction until the desired smoothness has been attained.

(b) Adjustment of the illuminating equipment :

Having switched on the lamp, set switching knob [2] to bright field [see para d] and open diaphragms [3 and 4]. A bright circle becomes visible on the protective plate. This circle can be observed without eye-piece or even better after detaching angular tube. By turning the side screws so as to be loosened and moving pull-rod (not shown in Fig. 2.1) in axial direction, the filament image is focussed on protective plate as much as possible. The pull-rod is then again clamped in position and the filament image is centred by actuating centring screws [5].

(c) Coordination of concave mirror condensers :

The coordination of concave mirror condensers to the objectives is to be followed according to the instructions of the manufacturer. The concave mirror and slide especially adapted for objective 25 x /0.50 are marked with black point and those for objective 50 x /0.80 with a white point. The following magnification values refer to the equipment of carrier VERTIVAL (factor 0.63 x) with angular tube (1.6 x) and monocular or binocular (1 x).

TABLE - 2.1

Magnification of microscope for different objectives and eyepieces

Objectives	Concave Mirror Condenser	Eyepiece			
		PK 8X	PK 10X	PK 12.5X	PK 16X
6.3x/0.12	11	50 X	63 X	80 X	100 X
12.5x/0.25	12	100 X	125 X	160 X	200 X
25 x /0.50	12	200 X	250 X	320 X	400 X
50 x /0.80	12	400 X	500 X	630 X	800 X
HI 100 x/1.30	-	800 X	1000 X	1250 X	1600 X

(d) Bright field (Fig. 2.2) :

For carrying out examination of a specimen in bright field the switching knob [2] has to be turned until the point to be found onto it does no longer face the observer. Attention should be paid to the diaphragm slide [6] with an arrangement for luminous field stop to bring it in centre being inserted in to the carrier to reach

the maximum insertion point for proper alignment. A green filter, an attenuation filter or a frosted glass may be introduced optionally or in a combined form into the filter slide [7]. This slide is provided with a free passage. Filter and shutter slides have to click indistinctly. The luminous field diaphragm is centred by actuating the two centring screws [8] and the aperture diaphragm by making use of socket wrenches to be put on to the two centring screws [9]. The image of the luminous field diaphragm is to be seen within the image of the objective sharply depicted and that of closed aperture diaphragm in the exist pupil of the objective after having removed the eyepiece.

(e) Dark field (Fig. 2.3) :

For investigations in the dark field the objective corresponding to desired magnification has to be fitted with the concave mirror condenser coordinated to it as mentioned above in (c). Switching knob [2] has to be set in such a way that the point to be found on it faces the observer. The luminous - field and aperture diaphragm are opened completely by actuating knurled rings [3 and 4].

(f) Camera attachment (Fig. 2.4) :

For taking photomicrographs of samples, camera is attached to the microscope. The arrangement is shown in Fig. 2.4. The advantage of this method is that it is possible to observe the sample while taking photographs. Exposure times can be automatically controlled.

2.3 INDENTATION TECHNIQUE:

mhp 160 microhardness tester (Fig. 2.5).

The indenting device [19] and the threaded socket for objective [20] are mounted on a common carriage, which can be moved to and fro laterally by handle [21] in the slide [22] until it meets the stop. This makes it possible to place either the indenter device or the objective above the test specimen. The threaded socket also has a threaded collar for concave mirror condensers, so that the indentation can also be measured with peripheral dark field illumination.

A fitment is attached to the upper surface of the slide for mounting the microhardness tester in the corresponding mount of an upright incident light microscope. The indenter device is suspended from two springs, so that it is rather sensitive to vibrations, which are manifested by continuous or intermittent swings of the index line on the force scale. If the vibrations exceed the tolerable level or (what is rarely the case) have a frequency that is in resonance with the natural frequency of the microhardness tester, provision must be made for absorbing the vibrations of the microscope or else the latter must be set up in a part of building, subject to little vibrations. Otherwise, the necessarily inaccurate application of the force, on the one hand, and the boring action of indenter on the other would result in errors that might affect the hardness readings considerably.

Various diamond pyramidal indenters may be used with mhp 160 microhardness tester. The knoop pyramidal indenter with rhombic base is employed in the present investigation. It is kept in small screw top case when not in use. It

can be inserted into the tester mounting by means of a special clamp. A stud on the mounting and a corresponding slot in the indenter hold provide for correct alignment. The mhp 160 microhardness tester is a very sensitive instrument that requires careful handling. Dropping it will certainly result in ruining its adjustments. The microhardness tester should always be kept in a closed case when not in use to avoid dust settling on it. For optimum utilization of the tester detailed instructions for its adjustment, etc., are given below :

(1) Level the stage [14] by using a highly sensitive spirit level.

(2) Focus microscope (without microhardness tester) onto an object having strinking features or onto a centring cross. The object must be flawlessly prepared (naturally or artificially) and mounted on the object stage (use plane field achromatic objective and eyepiece with cross line or measuring rod).

(3) Move the object until striking features or intersection of centring cross coincides with eyepiece cross.

(4) Exchange upper tube section having eyepiece for special tube with eyepiece screw micrometer and adjust.

(5) By turning the centring screws [23 and 24] bring the apex of fixed (left) measuring arm of eyepiece screw micrometer to coincide with the striking features of object or centring cross. Both measuring arms form a cross (zero position) (Fig. 2.6).

(6) Remove the objective with its slide.

(7) Insert microhardness tester with diamond indenter.

(8) Now screw formerly used objective into microhardness tester and place it in observation position. Critically focus onto specimen.

(9) Centre the objective by turning setting screws [25 and 26] with socket wrench until the striking features of the object (or centring cross) is again coinciding with apex of fixed measuring arm of dashed figure in micrometer eyepiece (Fig. 2.6).

(10) Turn the knurled knob [27] in a counter-clockwise direction (Fig. 2.7) to lock the indenter.

(11) Move the change over slide to indenter position.

(12) Observe the horizontal bright index line of the load indicator in the eyepiece. If it is not seen, turn the rear knurled knob [28, Fig. 2.7] on microhardness tester until it is seen.

(13) Focus line, if necessary, by adjusting micrometer eyepiece.

(14) Turn the knurled knob until the index line coincides with horizontal line in the eyepiece. If the eyepiece be oblique to the line, turn eyepiece. This fixes the initial position of index line.

(15) Apply suitable load.

(16) Observe the upward motion of the index line within the image field.

(17) Observe with naked eye the tip of the indenter and simultaneously turn the fine motion knob of the microscope so that image of the tip is seen on the specimen.

(18) Now observe through eyepiece and turn fine motion knob so that the indenter just touches the specimen.

(19) When the indenter touches the specimen, the index line starts moving back. Turn the fine motion knob uniformly until the index line coincides with the original reference line for fixed desired time (15 sec. in the present study).

(20) Turn fine motion knob in reverse direction until the index line goes back to the same upward position.

(21) Now lower the stage considerably.

(22) Release the indenter by actuating knurled knob [27] in clockwise direction.

(23) Remove load.

(24) Move the indenter device to its operating position and lock it.

(25) Turn knurled knob, if necessary, so that bright index line coincides with the horizontal line in the eyepiece.

(26) Observe the indentation mark through eyepiece and measure the length of the indentation mark with micrometer eyepiece.

(27) Compute the hardness by using necessary formula.

2.4 SILVERING TECHNIQUE:

The crystal surfaces and/or optical flats have to be coated with a highly reflecting layer of silver both for microscopic and interferometric studies. The principle of this method is to thermally evaporate silver onto the specimen at a very low pressure.

A commercial vacuum coating unit 'Edwards 12 EA' (Fig. 2.8) was used for this purpose. The vacuum chamber was evacuated by a three stage silicon oil diffusion pump backed by an oil rotary pump. The vacuum at different stages was measured by the Pirani guage and Philips ionisation guage incorporated in the unit. The surfaces were thoroughly cleaned before deposition of silver. The cleaning process of surfaces depends very much on the nature of the surfaces. Optical flats were first cleaned with nitric acid, washed with water after applying soap and then hydrogen peroxide. Thereafter they were cleaned by rubbing with cotton wool till no breath figures were formed on breathing over them. Freshly cleaved crystal surfaces did not require any cleaving. Final cleaning was done by ionic bombardment in vacuum coating unit by means of a high tension discharge.

When the pressure was about 1×10^{-5} torr spectroscopically pure silver was evoporated from a molybdenum boat by passing a low tension high current. In order to protect the surfaces to be coated from receiving the vapours of burnt impurities while heating the boat, it was covered with an adjustable shutter. Silver was deposited for the required time by removing the shutter from above the boat. The specimens were then optically studied.

2.5 VICKERS PROJECTION MICROSCOPE:

Vickers projection microscope has been used for optical studies and is shown in Fig. 2.9. This is an inverted type of metallurgical microscope in which the specimen to be studied is placed in a movable stage above

the objective lens. The flexible illuminating system which can be used both for transmission and inflection photography consists of a powerful mercury lamp, pointolite or carbon arc lamp, a condenser and an aperture controlled iris diaphragm. For visual observations, an eyepiece with a reflector is pushed into the tube below the objective. This completes the normal microscope system. For photomicrography, a projection eyepiece is used and the final image is focussed on the projection screen after reflection from the projection mirror. A slight refocussing is, of course, necessary when the visual system is changed to the projection system. A total magnification X 25 to X 4550 can be attained in certain steps with this microscope.

2.6 CRYSTAL GROWING TECHNIQUES:

2.6.1 Introduction:

In recent years, interest in the growth of single crystals is accelerated. Single crystals are always needed for various studies of theoretical as well as practical interest. The fundamental theoretical studies like electrical and thermal conduction, magnetic resonance, hardness, surface structure, etc. can be more meaningful if carried out only on single crystals grown under controlled conditions. Apart from their importance in theoretical studies, single crystals are also finding increasing importance in a wide variety of practical applicatons e.g. in ferro-electrics, piezo-electrics, semiconductors, thermo-electrics, and in several other devices. They are also finding use as scintillators. Alkali halides are of considerable interest for use as

infrared window materials, particularly for transmission in the 10.6 μm range (Lasers).

2.6.2 Different Methods of Growing Crystals :

There are a number of methods which have been developed for growing single crystals of different types of materials. The classification of these method is as shown below :

(1) Growth from Solution :

(A) Growth from water solution :

(a) By progressively (regularly) varying the temperature (by lowering the temperature) to reduce the solubility and produce crystallization under controlled condition (e.g. inorganic salts such as alkali halides, Rochelle salt, EDT, ADP, etc.).

(b) At constant temperature (i) by progressively decreassing the amount of solvent by evaporating and (ii) by increasing the amount of solute.

(B) Growth from flux (e.g. metals and non-metals, ruby, barite etc.).

(C) Hydrothermal growth (calcite and zincite, etc.).

(D) High pressure growth (boron nitride).

(E) Growth by gel method.

(F) Growth by electrodeposition.

(2) Growth from melt :

a. Bridgman - Stock Barger method.

b. Zone melting method.

c. Verneuil flame fusion method.

d. Czocharlski - Kyropoulos method.

(3) Growth from vapour (Gas) phase :

(Chemical vapour transport method)

(silicon carbide, cadmium sulphide, lead sulphide, zinc telluride, lead telluride, etc.).

(4) By chemical decomposition.

(Koref hot-wire method)

(5) By strain anneal method.

(6) From high temperature solution :

(Growth from mica, tourmaline)

(7) From low temperature solution.

A survey of methods of growth suggests that almost 80 % of crystals grown are from the melt. There are several standard books available on the growth of crystals by different methods /1,7-14/.

'Growth from melt' has been found to be most successful method for growing large single crystals of several materials such as semiconducting materials, alkali halide materials etc. All the methods of growth from melt rely on cooling the charge below its freezing point.

The basic condition to be satisfied for the production of single crystals from melt is that a progressive freezing of the charge takes place in a controlled manner. In other words the solid-liquid interface moves in a controlled manner along the growth axis. The growth rate of the crystal is the rate at which this solid-liquid interface moves in a direction perpendicular to the interface.

Generally the growth of single crystals from melt is influenced by the growth rate, the temperature gradient along the solid and impurities. There are several factors which limit the application of this method.

(1) The method is applicable only when the substance melts congruently and without irrevesible decomposition.

(2) There should not be solid state phase transformation between the melting point and, the temperature to which the crystal will latter be cooled.

(3) The temperatures required in growing crystals directly from pure melt are usually higher than those required by other methods. For this purpose, the furnace design and temperature control are important. The selection of a suitable material for crucible or container of the molten substance at elevated temperatures without contamination is also important.

The present author used the Kyropoulos method to grow single crystals of sodium chloride, potassium chloride and potassium bromide from melt.

2.6.3 Kyropoulos Method :

This method was developed by Czocharalski /11/ in 1918

although it is sometimes named after Kyropoulos /12/ who worked on the technique in 1926.

It is a crystal - pulling technique describing the slow pulling of a crystal from melt. Essentially a small single crystal seed is dipped into the surface of the melt and slowly withdrawn at the rate at which the crystal solidifies, while remaining in contact with the melt. If suitable precautions (e.g. avoidance of thermal and mechanical fluctuations) are taken, the material withdrawn from the melt solidifies as a large single crystal. This method is slightly modified by employing rotation mechanism of seed to avoid radial temperature gradient and impurities. The water cooling system for seed is also employed to keep the temperature of seed slightly lower than that of melt. The crystals grown by this way is shown in Fig. 2.10. The dimensions of typical crystals are as follows :

NaCl :	L = 4.5 cm D = 3.8 cm	KCl :	L = 4.64 cm D = 3.8 cm	KBr :	L = 3.5 cm D = 3.0 cm

2.7 ANALYSIS OF STRAIGHT LINE PLOTS :

2.7.1 Introduction :

No physical measurement is absolutely correct. It is always associated with an error. The final result in an experiment is obtained after a computation involving different physical quantities which are measured in the course of the experiment. It depends on the refinements of the experimental techniques and on the method of treatment

given to different observations /15,16/. Relationship between different physical quantities in an experiment should be made as simple as possible, preferably linear and should be amenable to graphical analysis /16-19/.

In the present work, relations between hardness of synthetic single crystals of NaCl, KCl and KBr expressed by a hardness number and applied load or applied load and diagonal of indentation mark on a cleavage surface or a suitable combination of different physical quantities for obtaining a straight line etc. on cleavage surfaces under controlled conditions are graphically studied. Data are plotted on a graph with carefully chosen scales along the axes so that details are not bunched, together over a small range and are commensurate with accuracy and precision of observations of the variables along the axes so as to minimize the unwanted magnification of errors associated with each observation. In the present analysis of observations, linear relationships between different physical quantities exist or are created by having suitable combinations of these quantities. Obviously the plot between variables having linear relation is straight line. It is necessary to obtain the estimation of the best straight line. For this several methods are known. Out of these methods the author has followed the method based on statistical estimation. Hence this method of estimating best straight line is briefly described here.

2.7.2 Statistical estimation of best straight line :

There are two ways of estimating statistically the best straight line :

a) Regression of Y on X, and
b) Regreesion of X on Y.

In both these methods one variable is assumed to be free from errors.

Regression of Y on X : Here X is assumed to be free from errors and errors are associated with observations for Y. The best straight line is one for which the sum of the squares of the deviation of every point is a minimum and the straight line with a slope m_1 and intercept c is given by

$$y = m_1 x + c$$

where $$c = \bar{y} - m_1 \bar{x}$$

where $\bar{x}$ and $\bar{y}$ are the mean coordinates of all observations given by $\bar{x} = \frac{\sum x}{n}$, $\bar{y} = \frac{\sum y}{n}$ and

$$m_1 = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sum (x - \bar{x})^2}$$

In the language of statistics m_1 is called the regression coefficient of Y on X.

Regression of X on Y : It is also possible to obtain regression coefficient of X on Y by following the above general procedure and replacing 'x' by 'y'.

$$x = m_2 y + c$$

where $$c = \bar{x} - m_2 \bar{y}$$

and $\bar{x} = \frac{\sum x}{n}$, $\bar{y} = \frac{\sum y}{n}$ and

$$m_2 = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sum (y - \bar{y})^2} .$$

The condition for the best fit of straight line is that the correlation coefficient 'r' is given by

$$r = \sqrt{m_1 \, m_2} \, .$$

If r is $\pm$ 1, the correlation between x and y is perfectly linear. For positive value of r, the line has a positive slope and conversely.

In the present work the author has utilized, in various chapters the conditions expressed above for each straight line plot in such a way that the correlation coefficient 'r' is unity or is much nearer to unity.

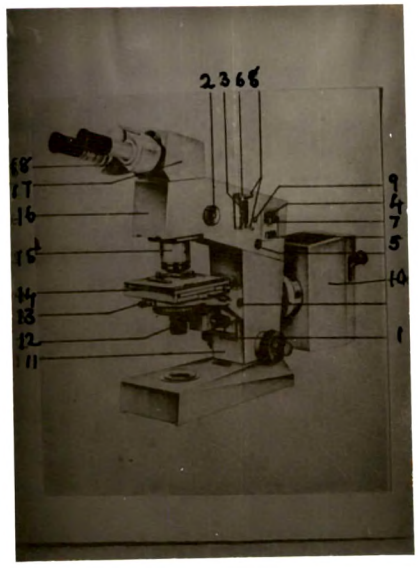

Fig. 2.1 Basic unit of VERTIVAL microscope

1. Pionion head.
2. Switching knob.
3,4 Diaphragm.
5. Central screws.
6. Diaphragm slide.
7. Filter slide.
8,9 Centring screws.
10. 12/50 lamp adopter.
11. Basic stand for incident light.
12. Stage carrier.
13. Tightening screw.
14. Specimen table.
15. Objective on slide with concave mirror condenser.
16. Carrier 'VERTIVAL'.
17. Angular tube.
18. Binocular straight tube.

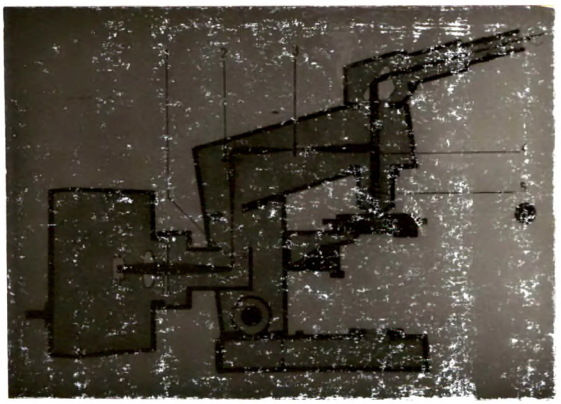

Fig.2.2 Ray diagram for bright field.

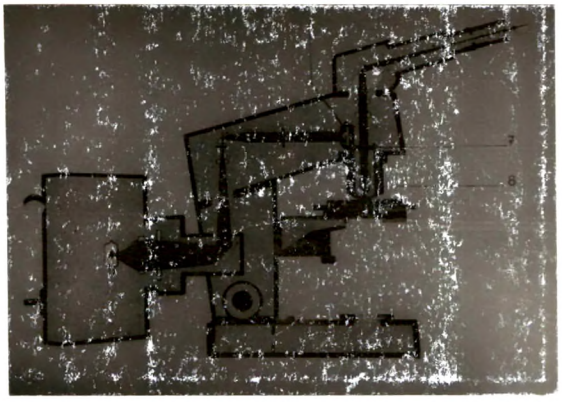

Fig. 2.3 Ray diagram for dark field.

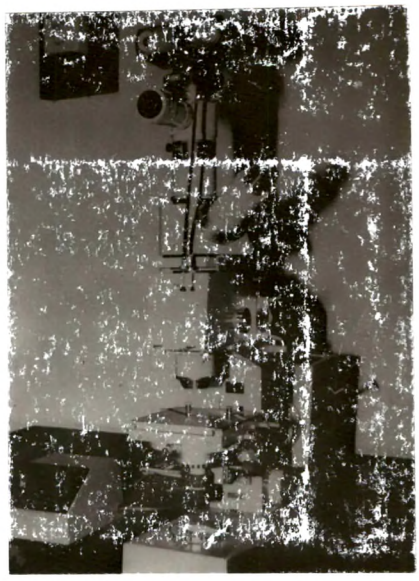

Fig. 2.4 Camera attachment on microscope for simultaneous observation and photomicrograph of specimen.

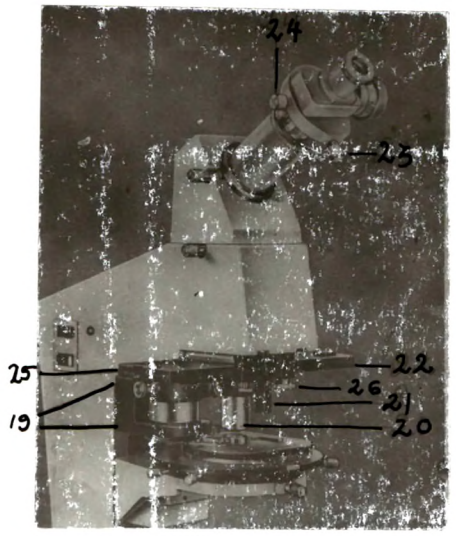

Fig. 2.5 Indentation Technique. mhp 160 Microhardness Tester.

19. Indentation device.
20. Objective.
21. Handle.
22. Slide.
23,24,25,26. Centring screws.

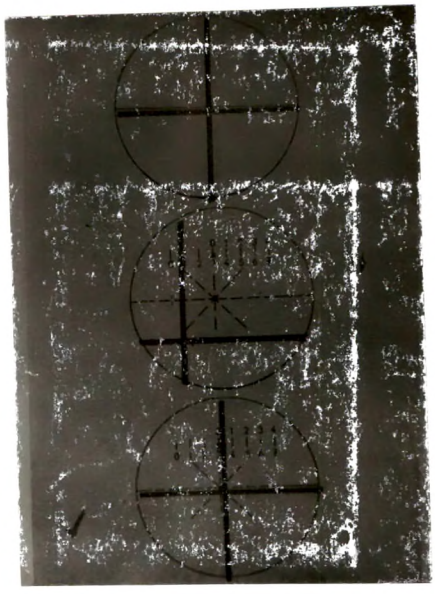

Fig. 2.6 Zero position of cross wire on graticule of micrometer eyepiece.

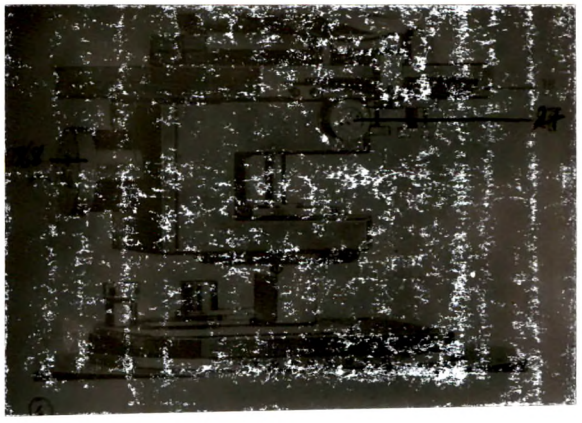

Fig. 2.7 Indentation technique.

27. Rear knurled knob for locking the indenter.

28. Rear knurled knob.

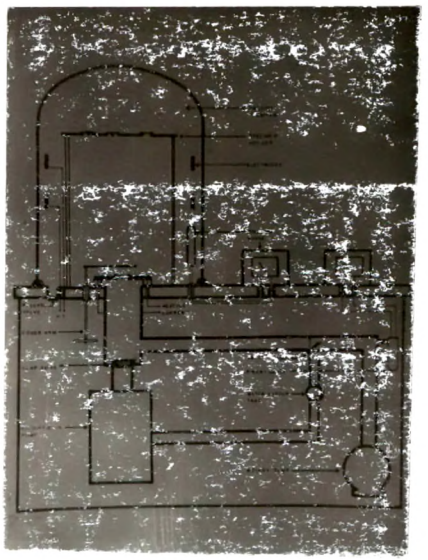

Fig. 2.8 Thermal Evaporation unit.

Fig. 2.9 Vickers Projection Microscope.

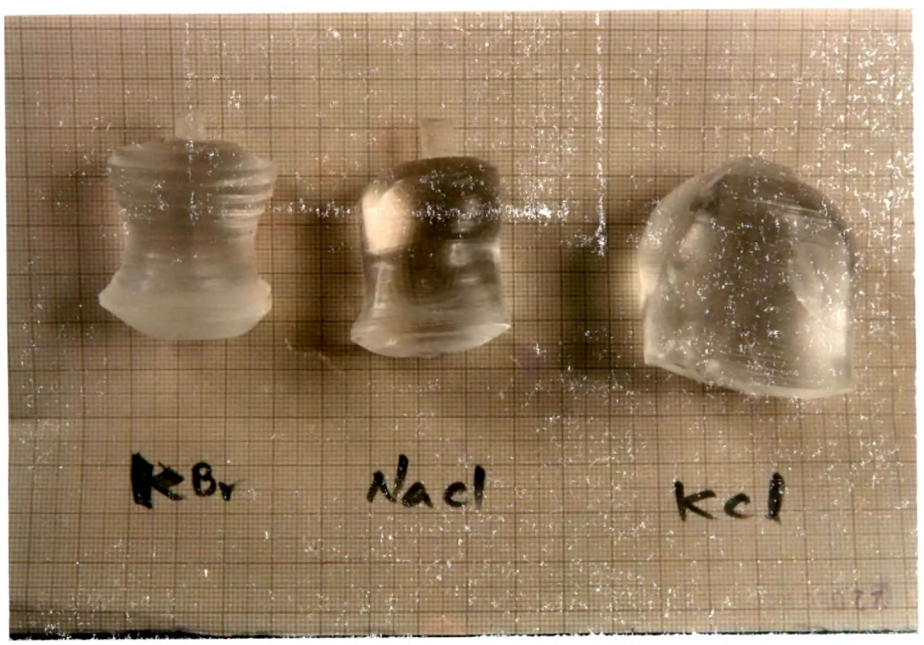

Fig. 2.10 Photograph of NaCl, KCl and KBr crystals grown by Kyropoulos method.

Crystal size NaCl : L=4.5 cm, D=3.8 cm KCl : L=4.6 cm, D=3.8 cm

KBr : L=3.5 cm, D=3.0 cm

R E F E R E N C E S

1. Gilman, J.J., 'The art and Science of Growing Single Crystals, John Wiley & Sons, Inc., N.Y., (1963).

2. Mott, B.W., 'Microindentation Hardness Testing', Butterworth Scientific Publications, London, Ch.I, (1965).

3. Martin, L.C. & Johnson, B.K., 'Practical Microscopy', Blackie Sons, London, IIIrd Edition, (1966).

4. Clark, G.L., 'The Encyclopedia of Microscopy', Reinhold Publication, N.Y., (1966).

5. Tolansky, S., Multiple-Beam Interferometry of Surfaces and Films, Cleardon Press, Oxford, (1948).

6. Worshnop, B.L. & Flint, H.T., 'Advanced Practical Physics' Methuen & Co., Ltd., London, (1971).

7. Buckley, H.E., 'Crystal Growth', John Wiley & Sons, Inc., N.Y., (1952).

8. Lawson, W.D. & Nelson, S., 'Preparation of Single Crystals', Butterworths, London, (1958).

9. Pamplin, B.R., 'Crystal Growth', Pergamon Press, Oxford, N.Y., (1975).

10. Henisch, H.K., 'Crystal Growth in Gels', Penn State University Press, University Park, Pa., USA, (1970).

11. Czocharalski, J., Quoted in 'Art and Science of Growing Crystals' by Gilman, J.J., John Wiley & Sons, Inc., N.Y., 321, (1963).

12. Kyropoulos, S., Quoted in Art and Science of Growing Crystals', By Gilman, J.J., John Wiley & Sons, Inc., N.Y., 413, (1963).

13. Holden, A. and Singer, P., 'Crystals and Crystal Growing', Doubleday and Co., Inc., N.Y., (1965).

14. Tarjan, I. & Matrai, M., 'Laboratory Manual of Crystal Growth', Akademiai Kiado, Budapest, (1972).

15. Brinkworth, B.J., 'An Introduction to Experimentation', The English Univ. Press Ltd., London, (1968).

16. Baird, D.C., Experimentation : An introduction to Measurement, Theory and Experiment Design'. Prentice - Hall, Inc., N.J., (1962).

17. Cook, N.H. & Rabinowiez, E., 'Physical Measurement and Analysis' Addition - Wesley, N.Y., (1963).

18. Topping, J., 'Errors of Observations and their Treatment', Chapman & Hall Ltd., London, (1955).

19. Knight, S.A., 'Understanding Graphs', Blackie & Sons, London, (1966).