# CHAPTER - 2

## CRYSTAL CHARACTERIZATION AND EXPERIMENTAL TECHNIQUES

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### Figures

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2.1 Crystal Characterization

Crystals are generally grown for two reasons: (i) to understand how crystals grow and (ii) for their scientific and technological uses. For both these reasons it is essential to evaluate quality of the crystals grown. There are no ideal crystals in reality, and all crystals grown by any technique contain some defects, impurities and inhomogeneities. Most of the physical properties are sensitive to deviation from the ideal ones. Therefore characterization of the grown crystals is essential.

Characterization is meant to include the full chemical and physical description of a material obtained from the whole spectrum of techniques. A crystal is characterized by description of its chemical composition, of its structure, of
its defects, and of the spatial distribution of these three features. Complete characterization should also include determination of electronic and excited states of the chemical constituents of the material. In addition, results of many physical measurements can help in a full description of a specific crystal. No crystal has ever been fully characterized; however, many crystals have been characterized to a point where relationship between their properties and the cation and concentration of their constituent atoms could be made. An excellent review on characterization has been compiled by a committee on characterization of materials, Materials Advisory Board, National Academy of Sciences, Washington D.C., 1967.¹

In this chapter a few well known techniques are described only briefly. Their full description is found elsewhere.² ³ Methods of characterization generally employed for zeolite crystals, and the experimental techniques used in the present investigation are also included in this chapter.
2.2 **Characterization of Zeolite Crystals**

The characterization and identification of complex, synthetic aluminosilicates, such as zeolites, is hindered by the absence of a definitive system of chemical nomenclature. Various systems of naming the synthetic zeolites, and other aluminosilicates have been employed by different investigators. These systems include: (i) Assigning to the synthetic species the name of the mineral relative if one such exists, based on a similarity in crystal structure as might be evidenced by similar X-ray powder patterns, (ii) Assigning to the synthetic zeolite species a code or letter designation.

Characterization of a previously unknown mineral or synthetic material, such as a zeolite, requires structural, compositional and physicochemical information to include,

(a) basic crystal structure as evidenced by X-ray diffraction,
(b) chemical composition and
(c) the chemical and physical properties which are characteristic of zeolites.
These include, dehydration behaviour, cation exchange behaviour and adsorption behaviour on gases and vapours. These properties reflect important structural differences that may not be adequately indicated by other means.

IR spectral studies on zeolites help in assigning the IR bands to certain structural groups in various zeolite frameworks. Conversely, presence of certain IR bands characteristic of zeolite frameworks can help in identifying new species as a zeolite. In order to conduct this assignment, it is necessary to know basic zeolite structure. Thus, IR method of investigation - in the case of zeolite crystals - is complementary to X-ray structural analysis.

2.3 Characterization of Crystal Surfaces

Since crystals grow or dissolve through the surfaces, a clue to solve problems of crystal growth should be found in the surface itself. There are several approaches to the study of surfaces but geometrical and structural investigations are the most fundamental ones.
Information that may be obtained through observations of crystal surfaces includes macro-morphology (crystal habit) and micro-morphology (surface microtopography) of crystals grown. Thus from detailed examination of crystal surfaces, one can obtain structural and environmental information in addition to information relating to the growth and dissolution process of crystals.

Surface structures of crystal faces represent only the final stage of crystal growth. However, it may be possible to reconstruct the whole process of growth by combining the observations on a large number of crystal faces. In general, interest in the surface microtopographical studies has been mainly focussed to understand the actual process of crystal growth.

2.4 Etching

A powerful method for investigating perfection of crystalline materials is the studies on etching of crystal faces. The individual grains, low angle grain boundaries and even individual dislocations can often be revealed by suitable solvents.
or etchants, that differentially attack the material. Impurities and other defects can also be revealed by the etching technique.

The exact mechanism by which an etchant may either remove the material uniformly or preferentially attack a dislocation is obscure in the case of most etches. Gilman et al.\textsuperscript{2}) and others\textsuperscript{3}) conclude that the first removal of an atom from the surface occurs where a dislocation intersects the surface. This is caused by the fact that strain energy and "core" energy cause atoms to be less tightly bond at the dislocation. Methods for establishing that an etch pit is associated with a dislocation are discussed by Laudise.\textsuperscript{4})

In the present investigation, to reveal dislocations and other imperfections existing in the crystals, etching technique was employed. Out of different methods of etching only one type, namely chemical etching, was employed in the present work. The details of this work are given in Chapter 5.

2.5 Vacuum Coating Unit

Crystal surfaces under examination were
coated with a layer of silver to enhance contrast. Silver coating unit, Edwards 12 EA, manufactured by Edward High Vacuum Co., used in the present investigation is shown in Fig. 2.1. It consists of a vacuum chamber in the form of a bell jar, 35.6 cm in diameter resting on an annular recess upon a gasket of neoprene rubber fitting on a metal base plate. The chamber is first evacuated with the rotary pump and the pressure recorded by a Pirani Gauge. When the pressure is about 0.2 torr, the chamber is connected to the three stage silicon oil diffusion pump, backed by a rotary pump. When the pressure of nearly $10^{-5}$ torr is reached, a molybdenum boat containing a couple of silver pellets is heated with a low tension high current. Silver vapour is allowed to deposit onto clean specimen surfaces, by turning away, for the required period, the shutter from over the boiling silver.

2.6 **Incident Light Microscope - 'Epignost'**

Almost all preliminary examinations of the crystal surfaces, as well as photographic recording of the observations at lower magnifications,
were carried out with the help of 'Epignost'. This microscope has been designed for rapid examination of the ground, polished, etched or natural surfaces of crystals. It affords every convenience called for in this kind of examination. Intended for low magnification only (a little under \(300 \times\)), it is accordingly provided with a coarse adjustment. Being an incident light type microscope, the objective has an infinite intersectional distance, i.e. the specimen lies in the focal plane of the objective and, its image is formed at infinity. The instrument contains a permanently built in tube lens which together with the eye-piece forms a telescope, thus resulting in a factor of 0.63 for calculating total magnification. A 6V, 15W filament lamp serves as the source of light.

The 'Epignost' can also be used for photomicrographic work. Specially suited for that purpose, is available the photomicrographic 'MF' equipment in combination with a miniature camera (Fig. 2.2). For the purpose of photography, the 'MF' tube is fitted to the tube carrier of the
2.7 **Multiple Beam Interferometry**

Multiple beam interferometry is a very sensitive technique for the study of crystal surfaces. It is developed by Tolansky. Although Fabry and Perot used a thin wedge silvered on both sides to produce sharp fringes, Tolansky was the first who investigated the critical conditions, to be fulfilled for a doubly silvered wedge, so that a close approximation to the Airy summation can be achieved. He has formulated the following conditions:

i) The surface must be coated with a highly reflecting film with a minimum adsorption.

ii) The film should contour the surface exactly and be highly uniform in thickness.

iii) Monochromatic light or almost a few widely spaced wavelengths should be used.

iv) The surfaces should be separated by a few wavelengths of light only.

v) A parallel beam within 1-3° tolerance
should be used.

Verma\textsuperscript{10)}, Forty\textsuperscript{11}) and Verma and Reynolds\textsuperscript{12}) used internal reflection interference fringes. Verma\textsuperscript{13}) utilized fringes of equal chromatic order to determine the step height of spirals in some cases, while Willis\textsuperscript{14}) and Joshi et al\textsuperscript{15}) exploited Fizeau fringes at geographic dispersion to study the properties of growth pyramids on quartz crystals.

Tolansky and Omar\textsuperscript{16}) used a thin film technique, where a drop of Canada balsam was placed in the form of a thin film with the help of cedar wood oil. They applied their method to flat surfaces, but very soon it was found that this technique did not suit for irregular surfaces. The irregularity of these surfaces demanded some physical interferometric technique. A suitable one "Improved Collodion thin film technique" was proposed by Joshi (1959).\textsuperscript{17}) This technique has been used in the present investigation and found to give good results.

With the help of this improved technique...
it is possible to increase the resolution to a high value and to obtain superb interferometric definition even at a magnification as high as X 2000.

2.8 X-ray Diffraction Studies

The physical perfection (position of atoms in a crystal) is equally important after the identity and quantity of the atoms present in a crystal, for crystal characterization. The beginning of such work is the accurate determination of structure of crystals (including microcrystalline substances) with X-rays. These techniques, based on monochromatic X-radiation, are generally more important because the d-spacings can be calculated from the observed diffraction angles. For microcrystalline synthetic zeolites and natural zeolites, X-ray powder diffraction methods are commonly used for the structural investigations and also for the purpose of identification. X-ray techniques used in the present investigation are presented below.

2.9 Philips X-ray Unit PW 1009

X-ray studies are carried out using Philips 100W X-ray generator type PW 1009 (Fig. 2.3).
This constant potential X-ray unit provides a high quality recording of diffraction spectra with all types of cameras. The degree of stabilization of the generator permits qualitative as well as semi-quantitative X-ray diffractometry. The shutter of the tube shield can be operated automatically by means of mechanical timers, type PW 1017. Also available is a magnetic water valve, type 1018, that automatically cuts off the water supply when the generator is switched off. The unit provides continuously adjustable high voltage in the range 0-55 KV and a stabilized tube current in the range 0-40 mA.

2.10 X-ray Diffractometer

Counter diffractometers have considerable advantages over film cameras and can give somewhat better precision. For microcrystalline synthetic zeolites, this method is commonly used. In these instruments, the diffracted radiation is detected by counter tubes, normally located at a greater distance, which move through the angular range of reflections. The intensities are recorded on synchronously advancing strip charts. An important feature of the diffractometer is its ability to focus, into a sharp
diffraction line, the radiation which is Bragg reflected from an extended specimen area. This as improves sensitivity as well/signal to noise ratio.

In the present investigation, the Bragg-Brentano diffractometer arrangement is used (Fig. 2.4). Here, use is made of the tendency of a divergent beam of X-rays to come to a "focus" after diffraction by the specimen. The specimen in the form of microcrystalline powder is mounted in the sample holder, which is then placed at the centre of the diffractometer and rotated by an angle \( \theta \) around an axis in the sample plane. The counter is attached to an arm rotating around the same axis by angles twice as large as those of the specimen rotation. Only (hkl) planes of the microcrystals parallel to the sample plane contribute to the diffracted intensity.

2.11 Infrared Studies

Infrared spectroscopy is undoubtedly a powerful technique available for elucidation of molecular structure and for qualitative and quantitative analysis. Infrared spectrum in the region of
200 to 4000 cm\(^{-1}\) is a sensitive tool indicating structural features of zeolite frameworks. It is possible to detect major structural groups present in zeolites from their infrared patterns.

Infrared transmission spectra were obtained using KBr wafer technique.\(^{18}\) A typical wafer concentration used was 2.0 mg of sample in 200 mg of KBr. Spectra in most of the cases were recorded with Perkin Elmer Model 180 double beam ratio recording null balance spectrophotometer. The spectral resolution is better than 5 cm\(^{-1}\) and the estimated accuracy is ± 5 cm\(^{-1}\). Spectra of at least two preparations of each sample were obtained before the spectrum was accepted as being characteristic of the zeolite species.

2.12 Electron Microscopic Techniques

Resolution possible with electron microscopy using a suitably controlled electron beam is superior to that of optical microscopy because of the shorter wavelength of electrons compared to that of light. An electron beam is focussed by means of magnetic fields and, is passed through
or is reflected from a specimen to a detector (often a fluorescent screen), a photographic plate or film or a solid state detector, where an image is detected. In 1949 Heidenreich showed that it was possible to produce thin sections of crystals by etching and he studied the structure of Al by transmission electron microscopy (TEM). It was also used by producing replicas for surface topographic studies. Heidenreich showed that thickness and orientation variations give rise to contrast effects which can be explained in terms of the theory of dynamical electron diffraction. In mid 1950's dislocations were observed with TEM and a whole variety of materials have been studied. Routine resolution of about 25 Å is common and a few Å are possible under optimum conditions. Information which can be obtained includes:

(i) Size, shape and distribution of particulate inclusions in crystals,
(ii) direct observation of lattice defects and strains, including slip lines,
(iii) Studies of dislocations and networks,
(iv) special technique modifications for the
study of, for example, magnetic domains.

In spite of its wide application, TEM still suffers from the complexities of sample preparation technique. The deficiencies of reflection electron microscopy are, to a large degree, caused by the difficulties of replica preparation. Many of these difficulties are eliminated by the scanning electron microscope (SEM).

In the SEM the focused spot produced by the electron source or gun is scanned across the specimen with a television type of raster by means of an electrostatic deflection system. Information about the specimen is obtained by detecting secondary electrons emitted from the specimen using a solid state detector. A photomultiplier signal is amplified and used to modulate the intensity of a synchronously scanned display tube to form a specimen image. Magnification is 400-400,000 X. To obtain topographs is a matter of minutes with a minimal sample preparation. The SEM has been operated in emissive, reflective, absorptive transmission and other modes depending on the material and problem at hand.
The principle of electron microprobe analysis is that of X-ray fluorescence. A beam of electrons is brought to focus on the specimen. Therein the electrons generate characteristic X-ray spectra. Commercial analytical instruments are provided with optics to analyse the emitted X-rays according to wavelength and intensity and, a viewing system such as an optical microscope to aid in selecting the exact area to be analysed. The fact that micrometer size areas can be moved systematically makes it an ideal mapping tool. Detectability limits are 100 - 500 ppm. Schematic diagram of an electron microprobe analyzer is shown in Fig. 2.5(a).

In the present investigation, scanning electron microscopy work and electron microprobe analysis were carried out on SEM Cambridge Stereoscan (S-4-10).

2.13 Philips EM 400

While working with an electron microscope one expects it to provide him with more information from his specimen than is available to him with current generation instruments. This extra
information could result from an improved specimen environment, better images from improved optical design, better instrument toleration of poor ambient conditions, faster working, better facilities for taking very good quality micrographs. All these improvements are achieved in Philips new model of electron microscope - EM 400 shown in Fig. 2.5(b).

The electron gun produces an extremely wide range of beam intensities at all accelerating voltages (from 20 KV to 120 KV in steps of 20 KV). Emission current can be varied in six steps between 2.5-100 $\mu$A. Highly coherent spots upto 0.2 um diameter can be formed on the specimen, using standard hairpin filaments. Final image is formed on a large fluorescent screen. Working pressures of the order of $10^{-7}$ torr are normally obtained in the vicinity of the specimen and the gun with negligible concentrations of hydrocarbons and water vapours. Clean pumping is carried out by an ion getter pump which evacuates the specimen chamber, the column and the gun chamber. This part of the system is virtually isolated from the viewing chamber, plate camera and, the rest of the volume
pumped by an oil diffusion pumping group with negligible back streaming properties, by a 200 um diameter diaphragm placed at the end of the lower tube at the level of the second projector lens.

A pre-aligned column (rigid and stiffened by the outer column wall), along with the ion-getter pump, support spine, viewing chamber and oil diffusion pump forms a single optical unit. This optical unit is vibrationally isolated from the microscope desk containing rest of the vacuum system, the electronics and high tension generator, by a rubber shock absorber. The optical unit consists of a system of seven lenses, of which two are condenser lenses, one objective lens, one diffraction lens, one intermediate lens and two projective lenses. The electron optical unit is surrounded by a magnetically-isolated outer wall of thick, soft iron which, while isolating the electron optics from magnetic influences, also shields the lenses from convection currents. For the maintenance of thermal stability all lenses are water cooled.

A 12 X binocular is attached for
critical focusing. A principal tilt up to $\pm 60^\circ$ and, a second tilt at right angles up to $\pm 30^\circ$ can be given to the specimen. Magnification facility can be used in three different ways. (i) EM 400 has 4.5 Å line resolution or 7 Å point resolution when $\pm 60^\circ$ high tilt goniometer is used giving maximum magnification 310000 X. (ii) It is possible to get 3.4 Å or 5 Å point resolution when $\pm 30^\circ$ goniometer is used giving high magnification up to 440000 X. (iii) Still higher magnification stage (800000 X) is possible for investigations where highest possible resolution (2.0 Å line, 3 Å point) is of prime importance.

A plate camera and a 35 mm roll film camera can be fitted so that a suitable camera can be chosen for each investigation. The cameras can be used up to 72 exposures and be stored under vacuum ready for use at any time. Selection of emulsion speed, exposure time and film transport are taken care of automatically. In the case of the plate camera the following information is printed automatically on each plate.

(i) Magnification or camera length (6 digits)
(ii) Accelerating voltage (1 digit code)
(iii) Exposure number (4 digits)
(iv) Operator identification (2 digit codes)

Energy dispersive analysis of X-rays (EDAX) and STEM unit also can be coupled to EM 400 for accurate chemical analysis and for different types of surface studies.

2.14 Luminescence Studies

Luminescence and the related electrical properties of the crystals are some of the striking effects that are brought about by the introduction of impurities. Further, luminescent properties are very much dependent on imperfections present in crystals. Thus, it is possible by luminescence studies to confirm presence of a particular impurity and its location in lattice sites of the crystals. The excitation and emission spectra can be examined by means of a spectrophotofluorometer.

2.15 Spectrophotofluorometer

In the present investigation Aminco-Bowman spectrophotofluorometer was used. It consists of an optical unit, photomultiplier tube,
The optical unit includes a Xenon lamp with housing and a blower, two monochromators, two slit holders (installed in monochromators), sample compartment, photomultiplier housing with manually operated rotatory slit turret and filter holder with shutter control. Xenon lamp power is supplied from the D.C. power supply, and the sweep power circuit is energized by a mercury battery contained within the optical unit.

Dispersion of light from the Xenon lamp is carried out by the excitation monochromator into monochromatic radiation incident on the sample. Emitted light from the sample is dispersed by a similar monochromator into monochromatic radiation incident on the photomultiplier. The light is then transformed to a weak electrical signal and fed to the photometer, where it is amplified. The photometer output is indicated on the self-contained meter. This output signal is connected to a strip chart recorder. The speed of the chart can be adjusted as per convenience. Excitation range of the instrument was 200 to 800nm.
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Captions of the Figures

Fig. 2.1 Edwards' Vacuum Coating Unit (Model 12 EA/617)

Fig. 2.2 Incident Light Microscope 'Epignost'

Fig. 2.3 Philips X-ray Unit PW-1009

Fig. 2.4 X-ray Diffractometer

Fig. 2.5(a) Schematic diagram of an electron microprobe analyser

Fig. 2.5(b) Philips EM 400