CHAPTER 3

CRYSTAL CHARACTERIZATION TECHNIQUES

People grow crystals for two main reasons: academic interest in the growth mechanisms and for scientific or technological utility of the grown crystals. For either of these purposes it is important to evaluate the quality of the crystals grown. The assessment of the physical and chemical perfection of materials has come to be called characterization. The United States National Academy of Sciences and National Academy of Engineering Committee of the Materials Advisory Board has defined characterization as follows[1]:

"Characterization describes those features of composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material".

This definition limits the characterization methods included herein to those that provide information about composition, structure, and defects and excludes those methods that yield information primarily related to material properties, such as thermal, electrical, and mechanical properties.

The techniques[2] used to characterize materials such as alloys, glasses, ceramics, organics, gases, inorganics, and so on are listed in Table 1. The microanalysis/structure[2] determination techniques applicable to inorganic solids: metals, alloys, semiconductors, are listed in Table 2 while the surface analysis techniques are listed in Table 3[2].

Apart from the techniques enlisted below, etching in conjunction with light microscopy continues to be a powerful (and relatively simple) tool in the study of the structure and defects of materials.

TABLE 1

Materials Characterization

Optical and X-ray Spectroscopy	a) Optical Emission Spectroscopy (OES) b) Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP- AES) c) Atomic Absorption Spectrometry(AAS) d) Ultraviolet/ Visible Absorption Spectroscopy (UV/VIS) e) Molecular Fluorescence Spectroscopy f) X-ray Spectrometry (XRS) g) Particle-Induced X-ray Emission h) Infrared Spectroscopy (IR FT-IR) i) Raman Spectroscopy
Mass Spectroscopy	a) Spark Source Mass Spectrometry b) Gas Analysis by Mass Spectrometry
Classical, Electrochemical, and Radiochemical Analysis	a) Classical Wet Analytical Chemistry b) Potentiometric Membrane Electrodes c) Voltammetry d) Electrogravimetry e) Electrometric titration f) Controlled-Potential Coulometry g) Elemental and Functional Group Analysis h) High Temperature Combustion(COMB) i) Inert Gas Fusion (IGF) j) Neutron Activation Analysis k) Radioanalysis
Metallographic Techniques	a) Optical Metallography (OM) b) Image Analysis (IA)
Diffraction Methods	a) X-ray Powder Diffraction (XRD) b) Single Crystal X-ray Diffraction c) Crystallographic Texture Measurement and Analysis d) X-ray Topography e) X-ray Diffraction Residual Stress Techniques f) Radial Distribution Function Analysis g) Small-Angle X-ray and Neutron Scattering

	h) Extended X-ray Absorption Fine Structure i) Neutron Diffraction
Electron Optical Methods	a) Analytical Transmission Electron Microscopy (TEM) b) Scanning Electron Microscopy (SEM) c) Electron Probe X-ray Microanalysis (EPMA) d) Low-Energy Electron Diffraction (LEED)
Electron or X-ray spectroscopic Methods	a) Auger Electron Spectroscopy (AES) b) X-ray Photon Spectroscopy (XPS)
Methods Based on Sputtering or Scattering Phenomena	a) Field Ion Microscopy and Atom Probe Microanalysis (FIM) b) Low-EnergyIon-Scattering Spectroscopy c) Secondary Ion Mass Spectroscopy (SIMS) d) Rutherford Backscattering Spectrometry
Chromatography	a) Gas Chromatography / Mass Spectrometry b) Liquid Chromatography c) Ion Chromatography
Resonance Methods	a) Electron Spin Resonance (ESR) b) Ferromagnetic Resonance c) Nuclear Magnetic Resonance(NMR) d) Mossbauer Spectroscopy

TABLE 2

Microanalysis/Structure

(The acronyms listed in Table-1 are used below)

Crystal Structure/ Phase ID	Phase Distribution / Morphology	Elemental	Defects
ESR TEM XRD	EPMA IA OM SEM TEM	AES EPMA SEM TEM	SEM TEM XRD

TABLE 3

Surface Analysis

Elemental	Molecular/Compound
a)Auger Electron Spectroscopy b)Rutherford Backscattering Spectometry c)Secondary Ion Mass Spectroscopy d)Low-Energy Ion Scattering Spectroscopy e)X-ray Photoelectron Spectroscopy	a) Infrared Spectroscopy b) Raman Spectroscopy c) Secondary Ion Mass Spectroscopy d) X-ray Photoelectron Spectroscopy

In the following sections compositional and structural characterization techniques are described.

X-RAY DIFFRACTION TECHNIQUES

X-ray diffraction is a tool for investigation of fine structure of matter. This technique had its beginnings in von Laue's discovery in 1912 that crystals diffract x-rays, the manner of the diffraction revealing the structure of the crystal. At first, x-ray diffraction was used only for the determination of crystal structure. Later on, however, other uses were developed and today the method is applied not only to structure determination, but to such diverse problems as chemical analysis and stress measurement, to the study of phase equilibria and the measurement of particle size, to determination of the orientation of a single crystal or the ensemble of orientations in a polycrystalline aggregate. X-ray diffraction techniques are some of the most useful in the characterization of crystalline materials, such as metals, intermetallics, ceramics, minerals, polymers, plastics or other inorganic or organic compounds. Most x-ray diffraction techniques are rapid and nondestructive. X-ray analysis is restricted to crystalline materials, although some information may be obtained on amorphous solid and liquids. The type of information desired may range from the question of sample crystallinity or its composition to details of the crystal structure or the state of orientation of the crystallites. Crystal structure analysis is usually performed only on samples of single crystals. Phase identification can be conducted on virtually all single crystal or powder samples. Also useful are measurements of the physical state of a sample that detect difference from the ideal crystal. The most common cause of crystal defects is deformation due to local or external applied stresses. Deformation or strain analysis is useful, especially in metallurgy.

Table 4 lists types of x-ray diffraction analysis, indicates specific technique and describes the required form of the sample.

TABLE 4

X-ray Diffraction Analysis

Types of analysis	Method	Sample
Crystal geometry	Moving crystal-spot pattern Computer positioned diffractometer Solution of d-spacing equations	Single crystal Single crystal Powder
Arrangement of atoms	Analysis of diffracted intensities Refinement of whole pattern	Single crystal Powder
Symmetry	Moving crystal-spot pattern Stationary crystal-spot pattern	Single crystal Single crystal
Identification of compound	Identification of cell parameters Matching of d-I set	Single crystal Powder
Crystal orientation	Single-crystal back reflection Laue Texture analysis	Large single crystal Powder compact
Size of the crystal	Line broadening	Powder
Magnitude of strain	Line shifts	Powder compact
Amount of phase	Quantitative analysis	Powder
Change of state	Special atmosphere chambers	Single crystal or powder
Crystal perfection	Direct imaging Line shape analysis	Single crystal Powder

The techniques used in the present investigation are detailed below.

X-RAY POWDER DIFFRACTION

A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the use of diffraction method for chemical analysis. X-ray powder diffraction (XRPD) techniques are used to characterize samples in the form of loose powders or aggregates of finely divided material. Qualitative analysis for a particular substance is accomplished by identification of the diffraction pattern of that substance. Quantitative analysis is also possible, because the intensities of the diffraction lines due to one phase of a mixture depend on the proportion of that phase in the specimen.

The powder method is best known for its use as a phase characterization tool partly because it can routinely differentiate between phases having the same chemical composition but different crystal structure (polymorphs). As a result, the diffraction method has been widely applied for the materials analysis.

In the XRPD technique, the powder sample is placed in a collimated monochromatic beam of x-radiation. The technique usually requires some sample preparation. This may involve crushing the sample to fit inside a glass capillary tube, rolling it into a very thin rod shape for the Debye-Scherrer camera technique, spreading it as a thin layer on a sample holder or packing it into a sample holder of a certain size. In some cases, the preparation would depend on the equipment available and the nature of examination. A diffraction pattern can be recorded on a photographic film, or by use of analog or digital methods. In any case, the final data can be displayed as a graph of intensity as a function of interplanar distance d, or as a function of diffraction angle 2θ. Many modern automated powder diffractometers can provide further data reduction, including peak finding a tabular listing of peak intensity versus interplanar spacing employing search/match software and other computer utilities.

Phase identification using XRPD is based on the unique pattern produced by every crystalline phase. Much as a fingerprint is unique for each person, the diffraction pattern can act as an empirical fingerprint for that phase and qualitative identification of phase can be accomplished by pattern-recognition methods that include established manual techniques and the newer method that use computers, most of which implement programs based on heuristic algorithms. All of these methods make use of the database maintained by the JCPDS international centre of Diffraction Data[3].

There are two different designs of diffractometers used for obtaining XRD pattern of powder samples and thin films.

The first one is "The Bragg-Brentano X-ray diffractometer". Here the specimen is mounted in the centre of the diffractometer and rotated by an angle θ around an axis in the film plane. The counter is attached to an arm rotating around the specimen axis by angle twice as large as those of the specimen rotation. Only (hkl) planes parallel to the film plane contributes to the diffraction intensity. The effective thickness of a film 't' decreases with increasing diffraction angle. Therefore the effective thickness of a film in 100 nm thickness range is sufficient to excite measurable diffracted radiation of small angles but the intensity falls off rapidly for higher index reflections.

The second design of diffractometers utilizes the Seeman-Bohlin effect, in which the specimen and focussing circle remain stationary, while the detector tube moves along the circumference of the focussing circle itself. Its main advantage is the constant angle of incidence, which can be kept as small as 5°, thus giving higher diffracted intensities than those obtained by Bragg-Brentano diffractometer in the whole angular range and particularly in the back reflection region.

However, in the present case diffractometer based on Bragg effect is used. The details of the diffractometer used are given in Chapter 9.

CRYSTALLITE SIZE

Metals and alloys are usually produced and used in the form of polycrystalline aggregates, composed of a great many individual crystals usually of microscopic size. Because the properties of such aggregates are of great technological importance, they have been intensively studied in many ways. The structure of the aggregate, in its broadest sense, means the relative size, quality, and orientation of the grains making up the aggregate. The fact whether these grains are large or small, strained or unstrained, oriented at random or in some particular way, frequently has very important effects on the properties of the material, the best known being the increase in the strength and hardness which accompanies a decrease in grain size. The grain sizes range from about 1000 to 1 μm. The most accurate method of measuring grain size in this range is by microscopic examination. Although x-ray diffraction is decidedly inferior to microscopic examination in the accurate measurement of grain size, one diffraction photograph can yield semi-quantitative information about grain size, together with information about crystal quality and orientation. A transmission or back reflection pinhole photograph made with filtered radiation is best. However, when the size of the individual crystals is less than about 0.1μm (1000 Å), the term "particle size" is usually used. Crystals in this size range cause the broadening of the diffraction curve which increases as the thickness of the crystal. The width B is usually measured, in radians, at an intensity equal to half the maximum intensity. As a rough measure of β, we can take half the difference between the two extreme angles at which the intensity is zero, which amounts to assuming that the diffraction line is triangular in shape. Therefore

$$\beta = (2\theta_1 - 2\theta_2)/2 = \theta_1 - \theta_2.$$

The Scherrer's formula[4] is used to estimate the particle size of very small crystals from the measured width of their diffraction curves:

$$D = 0.9\lambda/\beta\cos\theta$$

where β = broadening of diffraction line measured at half its maximum intensity (radians) and D = diameter of crystal particle This technique has been used to evaluate the particle size of the polycrystalline $BiSbTe_3$ films and the effect of heat treatment on the optical absorption of the films has been explained in terms of increase in the particle size. The detailed discussion is given in Chapter 13.

X-RAY SPECTROMETRY

While X-ray diffraction discloses various compounds and phases present in the sample, X-ray spectrometry gives information about the chemical elements present in the sample, irrespective of their state of chemical combination or the phases in which they exist. Chemical analysis by X-ray spectrometry can be either qualitative, if the various characteristic lines in the emitted spectrum are simply identified, or quantitative, if the intensities of these lines are compared with the intensities of lines from a suitable standard.

The analysis can be carried out in an x-ray spectrometer in either of the following ways:

1) Wavelength – Dispersive

   The radiation emitted by the sample is diffracted by lattice planes of known d spacing in a single crystal. In accordance with the Bragg law, radiation of only a single wavelength is reflected for each angular setting of the crystal and the intensity of this radiation can be measured with a suitable counter. A wavelength dispersive spectrometer is also called a crystal spectrometer.

2) Energy Dispersive

   In this spectrometer, diffraction is not involved. The various wavelengths in the radiation emitted by the sample are separated on the basis of their energies by means of a Si(Li) counter and a multichannel analyzer (MCA). This counter produces pulses proportional in height to the energies in the incident beam and the MCA then sorts out the various pulse heights.

Two kinds of x-ray spectrometry are possible, depending on the means used to excite the characteristic radiation of the elements in the sample:

1) X-ray excitation:

   The sample is bombarded with x-rays from an x-ray tube.

2) Electron excitation:

   The sample is bombarded with high-speed electrons in an evacuated apparatus.

Here we will describe only EDAX technique which has been used by the author.

ENERGY DISPERSIVE ANALYSIS OF X-RAYS (EDAX)

The technique EDAX is based on the simple concept of production of x-rays by elements. A beam of electrons about 0.5 μm in diameter is made to strike the specimen surface under investigation. The electron beam interacts with the atoms in the specimen to produce x-rays, which are characteristic of the specific atoms. The x-rays are analysed according to their energies. The generated x-rays are made to enter a liquid Nitrogen cooled Si diode detector doped with Li which intercepts the x-rays. The intercepted x-rays generate photoelectrons which eventually dissipate their energy by creating electron-hole pairs in the diode (which is reverse biased). These created electron hole pairs are separated by the junction to develop a voltage pulse signal. This voltage signal is proportional to the energy of the incident-rays and the number of pulses per second is a measure of the incident intensity of x-rays of that particular energy. Thus, the measurement of it after suitable amplification gives information about the energy of the x-rays incident. Thus, characteristic x-rays emitted by different species of atoms in the specimen can be identified by the measurement of number of voltage pulses and their magnitudes as functions of x-ray energy. As the Si diode detectors have a resolution of about 150 eV, the minimum energy that can be detected without overlap of the peaks is about 150 eV. This energy dispersive analysis of x-rays is less sensitive than the EPMA or WDAX by a factor of about 20. The EDAX is usually available with the Scanning Electron Microscope (SEM) where the electron beam falling on the specimen can also generate characteristic x-rays which can be analysed by EDAX using a silicon diode detector.

SECONDARY ION MASS SPECTROSCOPY

This is one of the methods which use sputtering phenomena. Due to its superior sensitivity, depth profiling and imaging capabilities, secondary ion mass spectrometry[5-7] (SIMS) is the most important chemical analytical technique that employs mass spectrometry to analyze solid samples. The fundamental basis of SIMS analyses is the measurement of the mass and intensity of secondary ions produced in a vacuum by sputtering the sample with energetic ion or neutral beams. The sputtering beam is referred to as the primary beam and typically has a kinetic energy of several thousand electronvolts. The primary beam removes atomic or molecular layers at a rate determined principally by the intensity, mass, energy of the primary species, and the physical and chemical characteristics of the sample. Sputtering of the sample produces a variety of particles including electrons, photons, atoms, atomic clusters, molecules, and molecular fragments. A small fraction of these sputter products are ionized, and these ions are the secondary ions in secondary ion mass spectrometry.

This method can be used to acquire a variety of information about the surface, near-surface, or bulk composition of the sample with high spatial and in-depth resolution, depending on the instrumental parameters. If the rate of sputtering is relatively low, a complete mass spectrum can be recorded to provide a surface analysis of the outermost 5 nm of the sample. This is often termed static SIMS. Alternatively, the intensity of one or more of the peaks in the mass spectrum can be continuously recorded at a higher sputtering rate to provide an in-depth concentration profile of the near-surface region. At very high sputtering rates, trace element or impurity analysis in the bulk is possible. Since the interpretation of SIMS spectra and depth profiles can be difficult; SIMS is not yet applicable for chemical analysis of unknowns. Further, the sputtering causes erosion or etching of the solid. But it has unique capabilities for answering specific questions about specimens whose stoichiometry and matrix structure are already characterized.

The detailed characterization study of Sb_2Te_3 and Sb_2Te_3-based crystals are given in Chapter 9.

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