 CHAPTER - 2
MATERIALS AND CHARACTERIZATION TECHNIQUES

This chapter outlines the brief introduction of two materials (Phlogopite mica and Muscovite mica) used in this thesis. It also gives the detail of source of irradiation used. Various characterization techniques employed to study the chemical composition, crystal structure and lattice parameters, thermoluminescence and dielectric properties have also been discussed in this chapter.

2.1. Materials used

Two types of micaceous minerals: Phlogopite mica and Muscovite mica have been used in the present study. Phlogopite mica belongs to the tri-octahedral category of micas while muscovite mica belongs to the di-octahedral category of micas. The detail of the materials used is discussed below.

2.1.1. Mica

Mica belongs to a family of minerals known as phyllosilicates in which the unit structure consists of one octahedral sheet (O) sandwiching between two opposite tetrahedral sheets (T) (Klockmann, 1978; Putnis, 1992). These sheets constitute a layer that is separated from adjacent layers (tetrahedral and octahedral) by planes of non-hydrated interlayer cations (I). The sequence becomes I TOT I TOT. The tetrahedral sheets have composition $T_2O_3$ and tetrahedra are connected by sharing each of three corners (basal atoms of oxygen) to a neighboring tetrahedron. The fourth corner (apical oxygen atom) directs in one direction for a given tetrahedral sheet. The coordinating anions around octahedrally coordinated cations (X) comprise apical oxygen atoms of adjacent tetrahedral sheets and anions A.

The simplified formula of mica can be written as

$$IX_{2-3}A_{1-10}T_4O_{11}A_2$$
where, \( I \) are the interlayer cations (e.g., Cs, K, Na, NH\(_4\), Rb, Ba and Ca), \( X \) are octahedrally coordinated cations (Li, Fe, Mg, Mn, Zn, Al, Cr, V and Ti), \( \Delta \) represents a vacancy, \( T \) is commonly Be, Al, B, Fe and Si, \( A \) is commonly Cl, F, OH, O and S.

There are three major divisions within the mica: a) the true micas, b) the brittle micas and c) the interlayer-deficient micas. These three divisions are further divided into dioctahedral (muscovite, boromuscovite, etc.) and trioctahedral groups (e.g. biotite and phlogopite) (Rieder et al., 1998).

2.1.1.1. Phlogopite Mica

In case of Phlogopite mica, the tetrahedron layer is a two dimensional network of edge sharing Si\(_4\)O\(_4\) tetrahedra with partial substitution of Si by Al and the octahedron layer is a two dimensional network of corner sharing Mg\(_6\)O\(_3\) octahedra. An octahedron sheet is sandwiched between two tetrahedron sheets and forms the TOT unit. The TOT units are weakly held together by electrostatic forces, mediated by shared non-hydrated interlayer K\(^+\) cations. In Phlogopite mica, all possible octahedron cation sites are occupied with Mg\(^{2+}\). Thus, the chemical formula of Phlogopite mica becomes K(Mg)\(_3\)AlSi\(_3\)O\(_{10}\)(F, OH)\(_2\). It is a yellow, greenish or reddish brown category of the mica. It is also known as dark mica.

2.1.1.2. Muscovite Mica

The muscovite mica consists of infinite tetrahedral sheets of corner-shared Si\(_4\)O\(_4\), with the apical oxygen atoms located at the corners of a hexagon. In the structure of muscovite mica, one-fourth of the Si is replaced by Al, with the remaining K\(^+\) and Al\(^{3+}\) ions lying between the aluminosilicate sheets. A single octahedral AlO\(_6\) sheet is sandwiched between two tetrahedral sheets, with a layer of K\(^+\) ions located between the trilayer aluminosilicate sheets. Since the ionic bonding between the K\(^+\) layers and the trilayer aluminosilicate sheet is weak, it cleaves rather easily at the positions of the K\(^+\) layers. Thus, the TOT units of muscovite is made up of the same two tetrahedron Si\(_4\)O\(_4\) subunits as in phlogopite but the octahedron subunit in case of muscovite mica consists of AlO\(_6\) octahedra. All (three out of three) possible octahedron cation sites are occupied by Mg\(^{2+}\) in phlogopite (tri-octahedral mica), whereas only two out of three octahedrons are engaged with Al\(^{3+}\) cations in muscovite (di-octahedral mica). Thus, the chemical
formula of muscovite mica becomes $\text{K(Al)}_2\text{AlSi}_3\text{O}_{10}(\text{F, OH})_2$. It is anisotropic in nature and its crystal system is monoclinic. It is also called white mica.

2.2. Source of irradiation

2.2.1. $\text{Co}^{60}$ Gamma source

A gamma chamber 1200 unit (GC 1200) (calibrated by Board of Radiation and Isotope Technology, Mumbai, India and installed at Inter University Accelerator Centre, New Delhi, India) with a $\text{Co}^{60}$ gamma source was used to expose the samples to gamma rays (Figure 2.1). The set-up of the gamma chamber mainly consists a radiation source, radiation shield for the source, central drawer including the sample chamber, driving system, control panel and an external cabinet.

The gamma chamber is a compact unit enabling an irradiation volume of approximately 1000 cm$^3$. The central drawer can be raised or lowered as required by a steel rope passing over a geared motor. This movement is controlled from the front panel through an electrical circuit by two types of programs, one is auto mode and other is manual mode. In manual mode, it will be operated manually and in auto mode, the required dose is fed on the screen and the samples will be irradiated automatically by raising and lowering in the gamma chamber to the given dose.

Figure 2.1: A photographic view of Gamma Chamber with $\text{Co}^{60}$ gamma source installed at IUAC, New Delhi, India.
2.3. Characterization Techniques

2.3.1. Electron Probe Micro analysis (EPMA)

Electron probe microanalysis (EPMA) is a nondestructive analytical technique widely used for determining the local composition and structure of heterogeneous materials such as alloys, thin films, minerals, ceramic, biological specimen, solid state circuits etc. (Reed, 1993; Mackenzie, 1993; Scott et al., 1995). EPMA is a spatially resolved, quantitative elemental analysis technique based on the generation and measurement of characteristic X-ray intensities emitted by a focused beam of energetic electrons (Castaing, 1951; Goldstein et al., 1981; Newbury et al., 1986). EPMA is able to measure the concentrations of elements (beryllium to the actinides) at levels as low as 100 parts per million (ppm). Electron probe micro analysis is very powerful tool because the properties and reactions of most of the materials depend not only on the average composition of the material but particularly on the localization of elements within the material.

2.3.1.1. Physical Basis of EPMA

When an energetic electron beam is incident on a sample, electrons interact repeatedly with the sample atoms until they come to rest or eject from the surface. In the keV energy range, the possible interactions of energetic electrons with atoms of sample are elastic scattering, inelastic collisions and bremsstrahlung emission (Salvat et al., 2004; Llovet et al., 2004). In Elastic scattering, the initial and final states of the atom are the same (normally the ground state). Elastic interactions cause significant angular deviation of the electron trajectories. In Inelastic collisions, the atom is brought to an excited state, i.e. a part of the electron’s kinetic energy is taken up by the atomic electrons. Inelastic scattering reduces the energy of the electrons and sets a limit to their range. Mechanisms of inelastic collisions include the production of secondary electrons, excitation of electrons in the conduction or valence bands, lattice vibrations (phonons), electron oscillations (plasmons), bremsstrahlung (continuum) X-rays and inner-shell ionization, i.e. the production of a vacancy in an inner-electron shell. Inner shell ionization occurs when the electron beam ejects a bound electron by transferring sufficient energy to the atom to exceed the binding energy of an electron of the atom.
The resulting atomic vacancy is then filled by a transition involving one or more outer shell electrons. The energy difference between shell levels can be demonstrated as an emitted characteristic X-rays or the energy can be transferred to another outer shell electron, which is ejected as an Auger electron. Inner-shell ionization is thus responsible for the emission of characteristic X-rays or Auger electrons. Because the energy of the atomic shells is sharply defined, the emitted characteristic X-ray or Auger electron has a defined energy and is therefore characteristic of the atom originally ionized by the electron beam.

The electron beam also produces X-rays when the electron is decelerated and loses energy in the electrostatic field of the specimen atom. The emitted X-rays are known as braking radiation or bremsstrahlung radiation. Since this energy loss can take any value from zero to the total energy carried by the energetic electron, the bremsstrahlung X-rays form a continuum background spanning all energies. Bremsstrahlung X-ray is indistinguishable from characteristic X-ray that may also occur at the same energy. Emitted photon (either as characteristic X-rays or bremsstrahlung) arises at sample depths ranging from the surface to some maximum depth, which depends on the material and on the energy of incident electron beam. Before emerging from the surface, generated X-rays can also interact with the target atoms through different phenomena (mainly photoelectric absorption) and as a result fluorescent X-rays may be emitted.

2.3.1.2. Instrumentation of EPMA

The EPMA instrument mainly consists of the electron microprobe column that contains an electron gun and an electromagnetic lens system. The electron gun acts as a source of electrons which upon heating produce electrons by thermionic emission. The filament is kept at negative potential to accelerate the electrons escaping from the filament. Typical accelerating voltages vary from 5-50keV. The electromagnetic lenses are used to focus the electron beam at the target atom within the diameter of about 0.1-1 μm. A virtual and visual beam system usually an optical microscope co-axial to the electron beam is commonly used for precise positioning of the specimen relative to the X-ray spectrometers. For this purpose, the beam can be scanned. Then, the images can
be generated by using the signal from an electron detector which generally detect low energy (secondary electrons) or high energy backscattered electrons from the sample. The EPMA instrument consists of several X-ray spectrometers, which can be energy dispersive X-ray spectrometers (EDS) and/or wavelength dispersive X-ray spectrometers (WDS). The wavelength (WDS) or energy dispersive spectrometer (EDS) contains an X-ray detector which is arranged in such a way that X-rays incident on the sample are diffracted according to Bragg’s law. The diffracted X-rays reach the detector and are recorded. A high vacuum system operating at pressures ranging from $10^{-4}$ to $10^{-6}$ Pa is generally used in order to prevent oxidation of the filament, breakdown of the accelerating voltage and scattering of the electrons in the beam. A computer system is used to control the beam, spectrometers, specimen stage, and quantitative data processing.

2.3.1.3. Instrumental specifications

The chemical composition of samples under investigation was analyzed using Cameca SX-100 Electron Probe Micro Analyzer (Figure 2.2) installed at Indian Institute of Technology, Roorkee, India. A thin sheet of samples was placed on sample holder and coated with layer of copper using sputtering unit to make the samples conducting. Then the coated samples were transferred to chamber of analyzer for elemental compositional measurements.

Figure 2.2: Photographic view of Electron Probe Micro analyzer at IIT, Roorkee, India.
2.3.2. X-Ray Diffraction (XRD)

The discovery of X-rays being diffracted by crystals provides a new tool to study the structure of materials. Since X-rays are electromagnetic radiation having wavelength of the order of 1 Å, X-Ray diffraction can give the detail of internal structure of materials up to an order of $10^{-8}$ cm. X-Ray Diffraction is a non-destructive analytical technique and has been extensively used for the determination of crystallinity, crystal structure, crystallite size, strain and lattice constants of the material. X-Ray diffraction (XRD) technique is based on observing the scattered intensity of X-rays hitting a sample as a function of incident and scattered angle (Cullity, 1959).

The most comprehensive description of scattering of X-rays from crystals is given by the dynamical theory of diffraction. Single-crystal X-ray diffraction is used to investigate the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules such as proteins. Powder diffraction XRD technique is used to study the crystallographic structure, crystallite size and preferred orientation in polycrystalline or powdered solid samples. Thin film diffraction and grazing incidence X-ray diffraction may be used to study crystallographic structure and preferred orientation of thin films. High resolution XRD is used to characterize thickness, crystallographic structure and strain in epitaxial films.

2.3.2.1. Physical basis of XRD

In X-ray diffraction technique, scattering occurs from large number of atomic planes. The scattered rays have definite phase relations and in most of the directions destructive interference occurs, but in certain directions where Bragg’s condition of diffraction is satisfied, constructive interference occurs. The basis of X-ray diffraction is best explained by Bragg’s equation which describes the condition for constructive interference for the scattered X-rays from the atomic planes of the crystal and is given by

$$n\lambda = 2d\sin\theta$$  \hspace{1cm} (2.1)
where \( n \) is an integer and represents the order of reflection, \( d \) is the spacing between atomic planes, \( \lambda \) is the X-ray wavelength and \( \theta \) is the angle that incident ray makes with the atomic planes. The incident rays satisfying equation (2.1) form the diffracted beam.

2.3.2.2. Instrumentation of XRD

The X-ray diffraction setup requires an X-ray source, the material under investigation and a detector to detect the diffracted X-rays. The X-rays most commonly used are those emitted by copper source, whose characteristic wavelength for the \( K_{\alpha} \) radiation is 1.54 Å. In \( \theta-2\theta \) scan mode, a monochromatic beam of X-ray is incident on the sample at an angle \( \theta \) with the sample surface and the diffraction occurs in every orientation of \( 2\theta \). The diffracted beam may be detected with the moving detector such as Geiger counter which is coupled with X-ray source in such a way that detector always makes an angle of \( 2\theta \) with the direction of incident X-ray beam. By scanning the material through a range of \( 2\theta \) angles, all possible diffraction directions can be obtained due to the random orientation of the material. The resultant diffraction pattern can be plotted between the intensity recorded by the detector and the angle \( 2\theta \).

2.3.2.3. Instrumental specifications

The X-Ray diffraction patterns of the samples under investigation were recorded using \( CuK_{\alpha} \) radiation (\( \lambda = 1.54 \) Å) from Shimadzu-7000 diffractometer (Figure 2.3) installed at Physics Department, Guru Nanak Dev University, Punjab, India with scan speed of 2 degree/min. The diffraction angle (\( 2\theta \)) was varied with the step size of 0.02°. The measurements have been done at room temperature under ambient pressure conditions.

2.4. TL Glow curve reader (Harshaw 3500TLD Reader)

The TL response of samples was studied on Harshaw 3500 TLD reader (Figure 2.4). It is a product of Harshaw Int., USA presently taken over by Thermo Electron Corporation, USA. The instrument is manually operated and has a sample drawer for a single element TLD dosimeter.
Figure 2.3: Photographic view of X-Ray Diffractometer at Physics Department, Guru Nanak Dev University, Punjab, India.

Figure 2.4: A Picture of TLD Reader at IUAC, New Delhi, India.
The sample was placed on a small heating plate of TLD reader (which also acts as a sample holder). It has a linear programmable heating system. A K-type thermocouple is fitted at the bottom of heating plate to measure the temperature and to maintain the heating rate. A thermoelectrically cooled Photomultiplier tube (PMT) is fixed above the heating plate with associated electronics to measure the TL output signal. TLD reader also contains a standard clear glass filter (a clean out/neutral density filter) to neutralize the non-linear response of the PMT. It operates on WinREMS Software that runs under Windows operating system on a computer, providing user friendly interface.

The external components of TLD reader include a front panel consisting of three LED lights, read push button, a sample drawer assembly which possesses an interchangeable planchet and a built in test light for periodic monitoring of reader performance and a drawer for neutral density filters. The rear panel houses a voltage selectable power input module and fuse access, a reset button, a fitting for nitrogen gas tubing, a RS-232-C serial communication port and a recessed pressure sensor adjusting screw.

The dosimetry functions are divided between the reader and the specialized TLD Shell Software that runs on the computer. All dosimetric data storage, instrument control and operator inputs are performed on the computer; signal acquisition and conditioning are performed in the reader. The Harshaw 3500 TLD reader uses contact heating with a closed loop feedback system that produces linearly sloped temperatures using a temperature controlled program. Its accuracy is within ± 1°C. The maximum temperature reachable in this reader is 400°C. The Time Temperature Profile (TTP) is user-defined in three segments: Preheat Acquire and Anneal, each with independent times and temperatures. It also has the facility for flowing nitrogen around the planchet. By eliminating oxygen in the planchet area, the nitrogen flow eliminates the unwanted oxygen-induced TL signals. Nitrogen is also routed through the Photomultiplier Tube (PMT) chamber to eliminate moisture caused by condensation. Beside the recorded glow curve, which appears on the computer screen, the data could also be stored in the form of ASCII files for its utilization in further analysis.
2.5. Dielectric Measurements

All the dielectric characterization was performed using NOVO-CONTROL (Alpha-A) High Performance Frequency Analyzer (Figure 2.5) in the frequency range of 0.1Hz to 10MHz installed at UGC-DAE consortium for scientific research, Indore, India. The theoretical dielectric analyses of the measured data were carried out using the WinFIT software from NovoControl. The basic concept of the theoretical approach (Havriliak Negami) is discussed in Chapter 1. The functioning of WinFit software developed for theoretical approach is discussed below.

Figure 2.5:  The Set up for Frequency analyzer at UGC-DAE Consortium for Scientific Research, Indore, India.

2.5.1. WinFIT Software

In modern measurement systems, the performance of the measurement system is mainly dependent on the quality of the software. For dielectric measurements, several software packages are available with different special aspects. There are several programs that control various analyzers. Some programs perform data evaluation or presentation. Data fitting is possible with the help of general mathematical software. In most cases, data formats of different applications are incompatible, so researchers have to convert data into required format using conversion programs. The procedure from the first measurement to the final plot involves a lot of time consuming steps with little
chances to automate these. In order to minimize this problem, NOVOCONTROL has
developed a software package specialized on dielectric analysis. The concept was to
create dielectric measurements and their evaluation with a high degree of
standardization and automatization. The NOVOCONTROL has been developed in close
coopération with researchers working on dielectric studies and therefore contains
nearly all features of practical importance. NOVOCONTROL includes the programs
WinDETA and WinFIT that are working in the user friendly MS-Windows
environment.

WinDETA executes the measurement control, basic data evaluation and data
representation. It supports ten of the most well-known impedance analyzers and three
temperature control systems for dielectric measurements. All devices are controlled by a
unique user interface and all the technical details are hidden in the software. The user
simply selects an actual device configuration. All other options of WinDETA like,
measurement control, data evaluation and data representation remain unchanged. The
feature of this concept is that measurements with different device combinations are
executed in standardized manner.

WinDETA supports value lists for the independent quantities frequency,
temperature, time and \( dc \) bias, which may be formatted in arbitrary order up to
measurements with five dimensions. In this configuration, WinDETA is capable to
perform a three dimensional frequency- temperature dependent measurement for each
point of the \( dc \) bias list. Temperature control is performed either manually or
automatically as a part of WinDETA’s measurement control. Heating or cooling rates
may be assigned. Therefore, the speed of the temperature difference between two points
can be specified. From the measured impedance data, all other dielectric quantities such
as the dielectric function, electric modulus, conductivity and so on are evaluated. These
data are exhibited in two or three dimensional representations. Data can be exported to
high resolution graphics or as ASCII tables.

In addition to two or three dimensional representations, WinFIT performs
analytic evaluations of the dielectric spectra \( \varepsilon^* = \varepsilon' - i\varepsilon'' \). The measured data can be
interactive graphically controlled. This includes deletion, shifting and insertion of data
points with the mouse, multiplication and connection of data curves being measured in various frequency ranges.

The main characteristic of WinFIT is non linear curve fitting of the measured dielectric data in the frequency domain. The fit function is Havriliak Negami Function given by the following equation

\begin{equation}
\varepsilon'(\omega) = -i \left( \frac{\sigma_{dc}}{\varepsilon_\infty \omega} \right)^{\alpha} + \left\{ \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i \omega \tau)^\beta} \right\} \quad (2.2)
\end{equation}

In this equation, \(\Delta \varepsilon\) is the difference in \(\varepsilon'\) at very low and infinite frequencies. \(\Delta \varepsilon\) is also proportional to the area under the maximum value or the relaxation peak of \(\varepsilon''\). The value of \(\varepsilon'\) at infinite frequencies is determined by \(\varepsilon_\infty\). \(\tau\) is the characteristic relaxation time. The width parameter \(\alpha\) depicts the broadness of the spectrum and gives the slope of the low frequency side of the relaxation in dielectric loss \(\varepsilon''\). The parameter \(\beta\) gives the asymmetry of the spectra and the value of \(-\alpha \beta\) gives the slope of the high frequency side of the \(\varepsilon''\) relaxation curve. Both the parameters \(\alpha\) and \(\beta\) are restrained to lie within 0 and 1. The Havriliak Negami equation includes the functions of Debye, Cole-Cole and Cole Davidson (Cole and Cole, 1941; Davidson and Cole; 1950, 1951). These functions can be fitted to the data in terms of the dielectric constant \(\varepsilon', \varepsilon''\), the conductivity \(\sigma', \sigma''\), the impedance \(Z', Z''\), the modulus \(M', M''\), the resistance \(R\), the capacity \(C\) and the loss factor \(\tan \delta\).

As WinFIT software was specially designed for Havriliak-Negami function, the performance of this software is very high. After completion of a fit, WinFIT offers an option to subtract the conductivity term of the fit function from the measured data. This allows displaying the measured spectra without the conductivity contribution. Generally, a series of frequency sweeps at various temperatures or other independent variables like time and \(dc\) bias is performed. Therefore, WinFIT allows to load a series of data measurements in the frequency domain. These series of spectra can be fitted automatically without the interaction of the user. All data are simultaneously displayed in a multi graphics window together with the fit functions and their single terms.
WinFIT also have an option for Master Plot, which scales all the spectra in the multi graphics window in such a way that the maximum in \( \varepsilon'' \) or \( M'' \) is located at 1 on the Y-axis and at frequency of 1 Hz at the X-axis. The user can easily switch between the normal scaling and master scaling. Also the conductivity term can be subtracted in the master plot representation.

Various file formats are supported by WinFIT. The data is imported either in the form of NOVOCONTROL WinDETA for DOS result files or in flexible ASCII format, which can be configured by the user. A complete series of fit results including data and fit functions can be saved and reloaded in single file with binary format.