CHAPTER-1

INTRODUCTION AND REVIEW OF LITERATURE

This chapter includes brief introduction about phyllosilicate minerals and their classification along with the applications of these minerals. The emphasis is given on the detail of the interaction of high energy ions and gamma radiation with matter. The relevant literature for the present study is also reviewed in this chapter. The motivation, aims and the objective of this thesis have been discussed in the last.

1.1. INTRODUCTION

There is increasing interest in radiation research and technology because ionizing radiation (such as X-rays, gamma rays, beta particles, alpha particles, etc) used in various fields like industry, nuclear power production, spacecraft power supply, medicine and insulation. Ionizing radiation has been found to be widely applicable in modifying the molecular structures and macroscopic properties of materials, and can be used to tailor the performance of either bulk materials or surfaces. Energetic charged particles on passing through the solids (dielectrics) lose their energy by excitation and ionization processes, and cause the radiation damage in materials along the path of the particle (Fleischer et al., 1965a). This radiation damage is also responsible for the changes in the structural, physical, optical and dielectric properties of the exposed material (Singh, 1999). Irradiation induced modification is a unique and very important technique used for modifying properties of material in a desired way. Swift heavy ion and gamma irradiation furnishes several interesting and utilitarian aspects in understanding the damage and material modifications to encourage its use for the development of insulating systems and dosimeter in radiation rich environment.

The silicate minerals form the largest fraction of most crustal rocks and, therefore, receive considerable attention due to its excellent properties. Phyllosilicates (sheet silicate or layered silicate) is a group of silicate minerals characterized by silicate (SiO$_4$) tetrahedral which are linked and arranged in the form of flat sheet. The group includes the mica and clay mineral groups. They are generally flaky, soft and of low density (Gaines et al., 1997; Deer et al., 2003). The phyllosilicates, as an important
class of valuable industrial minerals, play an essential role in many disciplines such as biotechnology, paper making, cosmetics, food processing, tailings management, and processing and utilization of natural resources (Yan et al., 2013). Some of the familiar known phyllosilicate minerals are phlogopite, muscovite and vermiculite. These were originally a waste product from minery, but their extraordinary electrical insulating properties and high thermal stability lead them to many applications (Hedrick, 2000). In addition to its main applications in insulation systems of high power rotating machines, these minerals are susceptible to ionizing radiation and are presently used as dosimeter for monitoring absorbed doses in radiation rich environments (Fleischer et al., 1975).

Irradiation of minerals can induce irreversible modifications of their macromolecular structure, in a controlled way, leading to remarkable changes in their structural, chemical, optical and electrical properties and leads them to several applications like solid state nuclear track detection (Fleischer et al., 1965b), microfiltering (Guo et al., 1988) and fission track dating in geology (Ahlem, 1980; Fleischer et al., 1964a), archeology, geochronology, gemstone enhancement, nuclear waste disposal and mineral exploration. The unusual properties of these minerals, i.e. their ability to be split into large, thin sheets that are uniquely useful for their electrical, thermal, and mechanical properties, high electrical and thermal insulating properties; resistant to chemical attack, the low dielectric loss and the excellent resistance against high temperature, make them valuable material for magnificent applications in opto-electric devices, insulation and radiation dosimetry.

Therefore, in the present thesis, the effect of heavy ions and gamma irradiation on optical, chemical, structural, dielectric and thermoluminescence properties of phyllosilicates mineral is carried out to identify and characterize radiation induced defects and its application in insulation and radiation dosimetry.

1.2. PHYLLOSILICATE MINERALS

Phyllosilicate minerals are the most abundant group of minerals and the most important rock forming minerals in earth’s crust (Nesse, 2012). Many phyllosilicates have been used as industrial materials due to their physical and chemical properties (Klein, 2002; Nesse, 2012). Since, the name phyllosilicates is derived from the Greek
word ‘PHYLLON’ which means ‘LEAF’ so they are also known as sheet or layered silicates (Gaines et al., 1997).

In general the phyllosilicate minerals are soft, have a good basal cleavage and low specific gravity and their great importance lies in the fact that they are the products of rock weathering and hence, the constituents of soils.

Phyllosilicate minerals comprise of tetrahedral ‘T’ and octahedral ‘O’ layers which are the basic building blocks of this group. A tetrahedral layer consists of silica (SiO₄) tetrahedral units. Within each unit, four oxygen atoms are arranged symmetrically around a silicon atom. Three out of 4 oxygens from each tetrahedra are shared with other tetrahedra. This leads to basic structural unit of Si₂O₅⁻² as shown in Figure 1.1. Successive tetrahedra are held together by shared apical oxygen atoms to form rings of tetrahedral ‘T’ layers. An octahedral unit consists of a central cation in a six fold co-ordination bonded to six hydroxyl groups, resulting in an octahedral symmetry. These hydroxyl groups are in turn linked to other surrounding metallic atoms (Ndlovu et al., 2013).

Figure 1.1: Basic structural unit of Si₂O₅⁻². (Taken from: Fraile et al., 2010)
Phyllosilicates accordingly are often differentiated as dioctahedral or trioctahedral based on octahedral occupancy. The trioctahedral phyllosilicate have divalent cations (mainly Fe$^{2+}$ or Mg$^{2+}$) in the octahedral sites and each octahedral site is occupied. Each oxygen of the trioctahedral micas is surrounded by and coordinated to three cations in adjacent, filled octahedral sites (Figure 1.2). For the dioctahedral phyllosilicate, trivalent cations in the octahedral sheets (generally Al, Fe$^{3+}$, or Cr$^{3+}$) are also bound to three oxygen or (OH)$^-$ groups, but to maintain charge balance one third of the octahedral sites are left empty, thus each oxygen or (OH)$^-$ group has cations in two adjoining octahedral (Figure 1.2). It is also an important group of minerals that includes the micas and the clay minerals (Ciullo, 1996).

![Figure 1.2: Trioctahedral layer and Dioctahedral layer. (Taken from: www.leorunfast.files.wordpress.com)](image)

1.3. MICA MINERALS

The micas are among the most abundant phyllosilicates used in the ceramic industry (Barlow and Manning, 1999). The name Mica was probably created from the Latin word ‘MICARE’ meaning ‘to SHINE’ in reference to the shiny luster of the Micas (Madhukar and Srivastava, 1995; Nesse, 2000).

Mica is a natural valuable mineral product applied to a group of complex aluminosilicate minerals having a sheet or plate like structure with different chemical compositions and physical properties. All micas form flat six sided mono clinical crystals with a remarkable cleavage in the direction of the large surfaces, which permits
them to split easily into optically flat thin sheets. When split into thin films, they remain tough & elastic even at high temperature (Sinkankas, 1969).

The structure of micas is stacked like a building with several different layers. Two tetrahedral layers (T) with their tetrahedral points pointing towards each other, sandwich small metal ions such as aluminium in an octahedral layer (O). This tetrahedral-octahedral-tetrahedral (TOT) sandwich is stacked with layers of large cations such as potassium or calcium. This cation layer is known as the interlayer (X) because it is between the (TOT) sandwich layers as shown in Figure 1.3. The whole structure can be illustrated with the following sequences of layers (Rieder et al., 1998).

X TOT X TOT X

![Mica structure](https://www4.nau.edu)

**Figure 1.3: Mica structure. (Taken from: www4.nau.edu)**

The tetrahedral sheets have composition T₂O₅ and tetrahedra are linked by sharing each of three corners (basal atoms of oxygen) to the neighbouring tetrahedron, fourth corner (apical atom of oxygen) points in one direction for a given tetrahedral sheet. The coordinating anions around octahedrally coordinated cations (M) consist of apical atoms of oxygen of adjacent tetrahedral sheets and anions A. The coordination of interlayer cations is twelve fold & their charge should not be less than 0.6 per formula.
Simplified formula for Mica

Reider have given general formula for mica group. This formula can be written as (Reider et al., 1998)

\[ XM_{2.3} (\ )_{1-0} T_4 O_{10} A_2 \]

Where \( X \) is Interlayer cations (Cs, K, Na, NH\(_4\), Rb, Ba, Ca),

\( M \) is an octahedral layer cation (Li, Fe (di or trivalent) Mg, Mn (di or trivalent), Zn, Al, Cr, V, Ti),

\( T \) is tetrahedral layer cations (Be, Al, B, Fe (trivalent), Si),

\( A \) is an anion Cl, F, OH, O (oxy micas), S),

(\( \)\(\))\(-\) represents a vacancy in octahedral layer.

The value of mica is in its unique physical properties. The crystalline structure of mica forms layers that can be split or delaminated into thin sheets. These sheets are flexible, elastic, platy, transparent to opaque, resilient, reflective, refractive, dielectric, chemically inert, insulating, lightweight, and hydrophilic. Mica also is stable when exposed to electricity, light, moisture, and extreme temperatures. Commercially important mica minerals are muscovite (potash or white mica) and phlogopite (magnesium or amber mica). Based on its greater abundance and superior electrical properties, muscovite is the principal mica used by industry. Muscovite products range in hue from colorless to pale green or ruby. Phlogopite remains stable at higher temperatures and is used in applications where a combination of high-heat stability and electrical properties is required. It ranges in color from pale yellow to light brown (Dana, 1857).

1.3.1. Applications of Mica Minerals

**Mica capacitors:** Mica is the oldest dielectric materials used in capacitor construction. Mica is very stable electrically, mechanically and chemically. It has a dielectric constant in the range 5-7. Because of its crystalline structure is asymmetrical mica is cleave into thin, optically flat sheets of 0.025-0.125mm. Muscovite mica is thermally stable up 500°C and Phlogopite mica is used up to 900°C (Kogel et al., 2006).
**Nano technology**: Mica is the almost first sample to be studied for the nanostructure formations induced by ion bombardments (Zhou *et al.*, 2013). Mica is used in nanotechnology i.e. nano wires, nanopores, nanofibres, quantum particles of different geometry.

**AFM**: Mica is commonly used as a substrate for AFM investigations or, as a calibration material and is known to be stable under contact mode atomic force microscopy. Due to these beneficial properties, mica has been considered a favorable material to explore ion-induced modifications (Ritter *et al.*, 2010).

**Paint**: Mica is used as a reflector, a pigment extender and for dry film reinforcement in paint. It gives the paint a glossy tone. It has high heat resistance. So the paint itself helps to insulate the home. It improves suspension stability, reduces checking & chalking and prevents shrinkage, blistering and shearing of the paint film provides increased resistance to water penetration, chemicals, and weathering and brightens the tone of colored pigments (Ciullo, 1996).

**Lubricants and greases**: Mica is greasy in nature. It is used in industrial lubricants to keep machine parts running smoothly. Mica is also used in textiles for lubrication of carding machines.

**Plastics**: Micas are used in plastics to improve electrical, thermal, and insulating properties. Mica is considered the most effective mineral for reducing warpage and increasing stiffness and heat deflection temperature in plastics. In general, mica reinforces crystalline better than amorphous polymers. Both muscovite and phlogopite micas are used in plastics, automotive, bath and shower, packaging, bumper, furniture, farm and lawn equipments, motor housing, coatings and sports equipment for their superior reinforcement properties (Ciullo, 1996).

**Coatings**: Mica sheets are used as a surface for carrying photographic films, as a protective covering for pictures and historical documents, mirrors of delicate physical instruments and for various optical purposes. It is used for packing and jackets of boilers and steam pipes. It also used for welding rod coatings.
**Makeup cosmetics:**- Mica is used in mineral makeup i.e. in eyeliner, eye shadows, lipsticks and shiner etc. Mineral makeup is good for sensitive skin, gives natural look and feel, stays on all day long and is an oil and fragrance free.

**Emergency lighting:**- Mica is used to separate electrical conductors in cable that are designed to have a fire resistance rating in order to prevent short circuits. So that cables remains operational during a fire.

**Electrical heating appliances:**- Armature coils, commutators heat sinks, invertors, Rectifiers, Rotating field coils, transformer, cigarette lighters, coffee percolators, curling irons, flat irons, hair dryers, hot plates, immersion heaters, and boilers, permanent wave machines, soldering iron machines, space heaters, steam iron press, toastees, vibrators, water heater, portable clothes dryers, branding irons, glue pots, laundry irons, lead pots, localized heating units, miscellaneous heating elements, thermostats (Kogel et al., 2006).

**Electrical control:**- Electrical & thermal regulators, grid resistances boxes, industrial motor starter, motor control panel, pyrometers, relays, Rheostat rods and terminals, starting boxes of trolley cars, Covers for fuse plugs, insulators, spark plugs for heavy duty compression engines, washers.

**Radio, radar, television etc:**- Bombarders, capacitors, Geiger-Muller counters, magnetic heads of computer, microwave windows, mosaic base and targets in iconoscopes, solid state application, transistor shields, tubes, Vacuum tubes, X-ray apparatus.

1.4. **CLAY MINERALS**

Clay minerals are a class of phyllosilicates which usually form as a result of chemical weathering of other silicate minerals at the surface of the earth (Zhang et al., 2010). Clay minerals are the most utilized minerals not just as the soils that grow plants for foods and garment, but a great range of applications, including oil absorbants, iron casting, animal feeds, pottery, china, pharmaceuticals, drilling fluids, waste water treatment, food preparation, paint, etc (Bergaya et al., 2006).
Clay minerals are an important group of phyllosilicates that are widely distributed in sedimentary rocks and occur in igneous and metamorphic rocks as alteration products (Martin et al., 1991). Many clay minerals are easily accessible and extractable anywhere in the world. Clay minerals have many specific and unique properties, some of which are useful in a number of industrial and technological applications, such as the manufacture of ceramics, as filling materials, as catalysts, as geologically datable material, and dosimeter (Choy et al., 2007). At present, clay minerals are used in numerous industrial branches, especially in ceramics, paper, rubber, plastics, chemical, agrochemical, dyes, foundry, and cement industries and as silicate binding materials, in pharmaceutic, cosmetic, food, petroleum industries, and in civil engineering and ecological projects (Grim, 1962; Konta, 1995).

Clay minerals are defined as those hydrous aluminosilicates that are characterized by crystal sizes less than 2 μm in diameter. Clay minerals are like micas, chlorites, and serpentes, characterized by a sheet structure made of layers of Si-O (± Al) tetrahedra (sharing 3 of their 4 oxygens), alternating with layers of octahedra or some other types of polyhedra of cations as Fe^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} with higher coordination numbers (Schulze, 2005).

Vermiculites are secondary 2:1 clay minerals (phyllosilicates) formed primarily by alteration of mica and less commonly by alteration of amphibole, chlorite, olivine, pyroxene or other clay minerals. The 2:1 layer is composed of one octahedral sheet between two tetrahedral sheets. The positive charge deficiency is compensated by the hydrated exchangeable cations Mg^{2+}, Ca^{2+}, Na^{2+} and K^{+} located in the interlayer space between the parallel 2:1 layers (Ritz et al., 2014).

Natural vermiculite is a constituent of the phyllosilicate or sheet silicate group of mineral including Al_{2}O_{3}, H_{2}O, MgO, FeO and SiO_{2}. Water located between layers is an important member in the vermiculite. It has high-level exfoliation property (Mathieson and Walker, 1954). Cation exchange capacity depends on the place and conditions of vermiculite formation. Generally, the value of layer charge is from 0.6 to 0.9 (Schulze, 2005).

Vermiculite is the most unique mineral in the world with a long history of applications in good insulation, fire resistance, advanced materials, building industry,
ceramics, agriculture, horticulture and industrial markets (Strand and Stewart, 1983; Hindman, 1992; Bergaya et al., 2006).

1.4.1. Applications of Vermiculite Mineral

**Insulation**: Vermiculite is used in thermal and acoustical insulation boards (e.g., ceiling tiles), lightweight insulating blocks, refractory blocks, and fire bricks. Coarse expanded vermiculite is used as loose fill insulation in interior building walls and with a silicone coating to minimize moisture absorption, in exterior walls (Hindman, 1992).

**Lightweight aggregate**: Vermiculite is used as an aggregate in ready-mix and preformed concrete to reduce weight and improve insulation properties. Of the alternatives (including pumice, pumicite, and perlite), vermiculite provides the lightest weight but physically weakest concrete (Bergaya et al., 2006).

**Agricultural products**: In decreasing order of volume consumed, the major agricultural uses of vermiculite are as a fertilizer carrier, in horticultural products, and as a soil conditioner. Expanded vermiculite will absorb fertilizer and trace nutrient liquids, and the resulting free-flowing particles provide controlled, slow release of these liquids to the soil. The low density, high absorption, and ion exchange properties of expanded vermiculite find use in potting, nursery, and farm soils. Exfoliated vermiculite provides a permeable soil structure having good aeration and water retention. It also controls the release of nutrients to the plant, and in nurseries it ensures a lightweight soil that facilitates the transplanting of large nursery stock. Expanded vermiculite is also used as a growing substrate in hydroponics, as a carrier of liquid additives, binder, anticaking agent, and digestive aid in animal feeds, and as an additive to manures to decrease their odor and improve their fertilizer value (Ciullo, 1996).

**Plaster and cement premixes**: Expanded vermiculite is used in ready-mix plasters and cements to impart low density, high thermal insulation, and low thermal conductivity. These mixes are sprayed on as lightweight, fire-resistant coatings for structural steel and concrete. The laminar nature of the mineral also protects against cracking and spalling of these coatings when subjected to temperature extremes and mechanical shock. Vermiculite is also used in fire protection boards at loading levels of
up to 90%. These boards are used as cladding for structural steel and in residential and commercial buildings as more aesthetic alternatives to sprays.

1.5. INTERACTION OF HIGH ENERGY IONS WITH MATTER

The interactions of ionizing radiation with matter always take place at the level of individual atoms. Accordingly, a single interaction can initiate a multiplicity of effects. Ionizing radiation may activate diverse physical and chemical effects in matter including heat generation, atomic displacements, electronic excitation of atoms and molecules, breaking of chemical bonds, and nuclear reactions. The specific effects depend on the type of radiation, the target, and the irradiation conditions.

When an energetic ion penetrates any material, it loses energy mainly by two independent processes:

(i) inelastic collisions of the highly charged projectile ion with the atomic electron of the matter, known as electronic energy loss ($S_e$).

(ii) elastic collisions with the nuclei of target atoms which is known as nuclear energy loss ($S_n$).

$S_n$ dominates at low energy (~1 KeV/amu), whereas $S_e$ dominates at high energy (1 MeV/amu or more). Both, the $S_e$ and $S_n$ of the ion depend on the energy and mass of ion. In the case of electronic interaction, it is pure coulombic, whereas it is screened coulombic potential for nuclear case. The energy loss of an ion is determined by the cross section of interaction between the ion and the target material along its trajectory. Thus, the total energy loss of swift heavy ions in matter is the sum of the electronic stopping power and the nuclear stopping power and is given by:

$$\frac{dE}{dx}_{\text{total}} = \left|\frac{dE}{dx}\right|_{\text{electronic}} + \left|\frac{dE}{dx}\right|_{\text{nuclear}}$$  \hspace{1cm} (1.1)

The mean value of energy loss $dE/dx$ for a large number of ions is termed as stopping power $S$, which is the sum of both the energy losses i.e. $S_e$ and $S_n$ (Durrani and Bull, 1987).

For a swift heavy ion moving at a velocity comparable to the Bohr velocity of the electron, the inelastic collision is the dominant mechanism for transfer of energy to
the material, which may produce tracks. In the inelastic collision, the energy is transferred from the projectile to the atoms through excitation and ionization of the surrounding electrons. The amount of $S_e$ in each collision varies from tens of eV to a few keV per Angstrom (Å), depending on ion mass and energy and also the material.

The variation of energy loss (both nuclear and electronic) of Ag ions with the energy of the ion in carbon is shown in Figure 1.4. There are three regions in the Figure as per different energy of the projectile. Region I is low energy region (1 keV/amu), where $S_n$ dominates over $S_e$. The ions within this range, loses their energy mainly via collisions with the target nuclei and transfer energy and momentum to the recoil atom. As a result of which, atom is displaced and the direction of the ion changes (elastic collision). In region II, $S_e$ increases with energy and reaches to a maximum value, after which it decreases with energy (region III). Region (II+III) is high energy region, here $S_e$ dominates over $S_n$ because at high energies, where the velocity of ion is comparable with the Bohr velocity of orbital electron, the ion interacts with the electrons of the target atoms (inelastic collisions), which results in excitation and ionization of the target atoms. Since the mass of the ion is much higher than the mass of the electron, the initial direction of the ion in the solid remains almost unchanged. The energy loss value for a given kinetic energy of an ion can be calculated for various targets by different stopping codes such as the “Stopping and Range of Ions in Matter” (SRIM) code (Ziegler and Biersack, 1999).

At low ion velocities, where the nuclear energy-loss dominates the energy loss process is correctly described by the electrostatic interaction between the projectile and the target atoms using a Thomas- Fermi potential (Ziegler et al., 1985). The radiation damage created by nuclear-energy-loss of ions is understood in terms of knock-on processes and cascades, in which the kinetic energy of an ion is directly transferred to the nucleus of a target atom. The damage trail is characterized by interstitial atoms and vacancies in the target due to elastic collisions.

For energetic ions (~1 MeV or more), the kinetic energy is first transferred to the electron of the target material. This leads to multiple ionization processes along the ion path and results in primary electrons with high kinetic energies (depending on the ion
energy). These electrons can release secondary electrons through coulomb interactions. Part of this excitation energy is directly converted into lattice vibrations (heat) and luminescence. Only a fraction (typically a few %) of the deposited energy results in radiation damage. The electronic energy losses at higher ion velocities are better described by the Bethe-Bloch formalism (Jackson, 1983; Durrani and Bull, 1987):

\[
-\frac{dE}{dx}_{\text{electronic}} = \frac{4\pi nZ_{\text{eff}}^2}{m_e} \left( \frac{e^2}{4\pi \varepsilon_0 \nu} \right)^2 \ln \left( \frac{2m_e c^2 \beta^2 W_{\text{max}}}{I \left(1 - \beta^2 \right)} \right) - 2\beta^2 - \delta - U \]  

(1.2)

The symbols are defined as:

- \( E \) ion energy
- \( x \) length of the ion path
- \( m_e \) mass of the electron (9.109×10^{-31} \text{ kg})
- \( c \) speed of light (2.998×10^8 \text{ m/s})
- \( n \) target electron density
- \( z \) charge of the ion
- \( \beta = \nu/c \) velocity of ions relative to the speed of light \( c \)
- \( \nu \) ion velocity
- \( e \) elementary charge (1.602×10^{-19} \text{ J})
- \( \varepsilon_0 \) Vacuum permittivity (8.854 ×10^{-12} \text{ C}^2/\text{Jm})
- \( I \) mean excitation potential of the target

Here \( \delta \) is a correction for polarization of the medium, important only at high energies, and \( U \) is a term which takes into account of the non participation of inner electron. Derived from perturbation theory of quantum-mechanics, the Bethe–Bloch formula is valid only for a completely ionized projectile. Here the effective charge of the ion has to be introduced because when passing through matter the ion constantly catches and loses electrons, and therefore changes its state of charge (Durrani and Bull, 1987).
1.5.1. Range of Ions in Solid

The projectile ion range in solid is defined as the mean depth from the target surface at which the ion comes to a halt. As the ion penetrates the surface, it slows down by transferring energy to both the electrons and the nuclei of the solid. It comes to rest after several tens or hundreds of nm, depending on its initial energy, the element number and the density of the solid. The range of an ion in a solid can be expressed by the rate of energy loss \( \frac{dE}{dx} \) along the trajectory of the ion.

\[
R = -\frac{E_0}{\frac{dE}{dx}} \left( \frac{dE}{dx} \right)^{-1} \, dE
\]  

(1.3)

where, \( E_0 \) is the incident ion energy at the target surface, \( x \) is the distance measured along the ion path, \( dE/dx \) is the energy loss (which has both nuclear and electronic energy loss part) of the ion with energy \( E \). \( R \) is the range of ion of energy \( E_0 \) (Kapoor and Ramamurthy, 1986; Durrani and Bull, 1987).
The energy loss phenomenon is statistical in nature as the collisions between projectile ions and target atoms are random. All ions penetrating the solid do not have the same penetration depth, but there is distribution along its path called longitudinal straggling. Since each successive collision of projectile ion with target atoms leads to deviation from its straight-line path resulting in a straggling in lateral direction called lateral straggling. In general, the range distribution for a particle injected into the surface of a target is defined as the probability density for finding the particle at rest at a given position inside the target at a later time. Statistical notations enters the description because the single ion is generally not representative for the experimental situation, where a beam of ions is injected and only the mean of many ions is observable.

1.5.2. Formation of Ion Tracks in Materials by Swift Heavy Ions

When the swift heavy ions pass through the target material the formation of damage zones in the material takes place. The material transforms into disordered state along the ion trajectory called latent track (damage zone created along the paths of swift heavy ions). The emergent of these tracks is the result of high local electronic energy deposition along the ion path. Basically, two different mechanisms named as Ion explosion or Coulomb explosion and thermal spike (Toulemonde et al., 1992) can be considered for track formation.

In the Coulomb-Explosion model, the damage creation process is described as a repulsion of positively charged target atoms close to the ion trajectory (Fleischer et al., 1965a; Lesueur and Dunlop, 1993). The ions transfer their kinetic energy to the target electrons. The electron cascade results in a trail of positively charged target atoms. It is obvious that the positive target atoms attract the free electrons and only if the charge neutralization time exceeds about $10^{-14}$ s (Johnson and Brown, 1982; Schiwietz et al., 2001) the repulsion of the positive target atoms can take place, creating an ion track consisting of interstitial atoms, vacancies, and other defect features. Later, neutralization of the ions and relaxation of the lattice occur, during which mechanical tension forms.

In thermal spike model, the energy of electronic excitation of the solid after the passage of an ion is transferred to the phonon system (lattice vibration) by electron-
phonon interactions. So, the energy is transformed into heat, which results in a strong increase of the temperature in a short time interval close to the ion trajectory. This temperature peak can lead to a melting process, and the defect creation and amorphisation are explained by the rapid cooling of the molten phase. Within the Thermal-Spike model the track diameter is defined by the extension of the cylindrical zone, in which the temperature is high enough for melting (Wang et al., 1994; Toulemonde et al., 1996a; Toulemonde et al., 1996b; Dufour et al., 1999; Toulemonde et al., 2000; Wang et al., 2000).

1.6. INTERACTIONS OF GAMMA RADIATION WITH MATTER

When gamma radiation passes through matter it may interact with the material, transferring some or all of its energy to the atoms of that material. Interaction of gamma radiation with matter depends upon many factors like mass, energy, atomic number, mass number and density of the medium. The interaction of gamma rays with matter is different from that of charged particles. The difference is apparent in the much greater penetration power of gamma rays and in the absorption laws. Gamma rays are electromagnetic radiations having no definite range. Unlike charged particles, a well collimated beam of gamma rays shows the exponential absorption in matter, this is because photons are absorbed or scattered in a single event. If the gamma radiation of intensity $I$ is incident upon an absorbing layer of thickness $dx$, the amount of radiation absorbed $dI$ is proportional both to $dx$ and the intensity $I$ such that

$$I = I_0 e^{-\mu x}$$

where $\mu$ is the linear absorption coefficient. The primary interactions of gamma rays with matter results in the production of energetic secondary charged particles usually electrons and it is these charged particles and their interaction with matter that accounts for the actual transfer of energy and detect of the ability of the initiating photon. The secondary particles produce most of the ionizing events; whereas as the primary photon is weakly ionizing.

There are number of processes which can cause gamma rays to be scattered or absorbed in matter, but only three main types which play an important role in radiation
measurements are photoelectric absorption, compton scattering and pair production. These effects are as follows:

### 1.6.1 Photoelectric Effect

The photoelectric effect results in the total destruction of the photon with the entire gamma ray energy being used up in the process of detaching an atomic electron from its parent atom and endowing it with kinetic energy (Liverhant, 1960).

The photoelectric absorption process involves an interaction between an incident photon and bound electron. In this process, a photon undergoes an interaction with an absorber atom in which the photon completely disappears. In its place, an energetic photoelectron is ejected by the atom from one of its bound shells. The interaction is with the atom as a whole and cannot take place with free electrons. For gamma rays of sufficient energy, the most probable origin of the photoelectron is the most tightly bound or K shell of the atom. If the incident photon has low energy compared to the binding energy then classical scattering occurs. If however, the incident photon has energy just greater than the binding energy of the electron, a complete transfer of the photon energy to the electron occurs which results in an escape of electron. A photon of energy $h \nu$ ejects a K shell electron of binding energy ($E_b$). The electron escapes from the atom with an energy $E_e$ equal to that of the incident photon minus the energy required to release it from its orbit.

$$E_e = h \nu - E_b$$

There is no scattered photon, all the energy has been transferred to the electron, known as photoelectron. Interactions of this kind can take place with electrons in the K, L, M, N shells. Since the photoelectric process results in the emission of an electron from a position in one of the shells of the atom, a vacant space is left in that shell. This vacant place is quickly filled through capture of a free electron from medium and/or rearrangement of the electrons from other shells of the atom. Therefore, one or more characteristics X-ray photons may also be generated. Although in some cases, the Auger electron may substitute for the characteristics X-ray in carrying away the atomic excitation energy.
The photoelectric process is the predominant mode of interaction for gamma rays of relatively low energy. The process is also enhanced for absorber materials of high atomic number $Z$. The probability of photoelectric absorption per atom over all ranges of $E_{\gamma}$ and $Z$ is

$$\tau \equiv \text{const.} \times \frac{Z^n}{E_{\gamma}^{3.5}} \quad (1.6)$$

where the exponent $n$ varies between 4 and 5 over the gamma ray energy region of interest. This dependence of the photoelectric absorption probability on the atomic number of the absorber is a primary reason for the preponderance of high $Z$ materials in gamma ray shields (Knoll, 1989).

### 1.6.2. Compton Scattering

The Compton effect is an inelastic scattering collision takes place between an incident gamma ray photon and an electron in the absorbing material. It is the predominant interaction mechanism for gamma ray energies typical of radioisotope sources.

In Compton scattering, the incoming gamma ray photon is deflected through an angle $\theta$ with respect to its original direction. The incident photon ($h\nu$) transfers a portion of its energy to the electron, known as Compton electron and the remainder of the energy appears as scattered photon ($h\nu'$) of lower energy.

$$h\nu' = \frac{h\nu}{1 + \frac{h\nu}{m_e c^2} \cos \theta} \quad (1.7)$$

Because all the angles of scattering are possible, the energy transferred to the electron can vary from zero to a large fraction of the gamma ray energy. In addition the greater the angle through which the photon is scattered, the longer is the wavelength of the scattered radiation. This scattered radiation is called modified scatter and the process is referred to as the inelastic scattering or Compton scattering. The proportion of photons scattered in the different directions varies with the energy of incident photon; low energy photons are scattered in all directions with almost equal probability, whilst high
energy photons (greater than about 1 MeV) are scattered primarily in the forward direction. The recoil electron behaves the same way as any electron. Since the recoil electron has been given kinetic energy, it can now undergo the various types of electronic particle interactions. It is indeed the recoil electron resulting from the Compton collision which causes the radiation damage to the materials, not the initial photon interaction which has created only one ion directly. The probability of Compton scattering per atom is increase linearly with atomic number \( Z \) as it depends on the number of electrons available as scattering targets (Liverhant, 1960; Kapoor and Ramamurthy, 1986; Knoll, 1989).

1.6.3. Pair Production

Pair production results in the complete absorption of the gamma radiation quantum which is converted entirely into rest energy of the electron pair (a positron and a negative electron) plus a certain amount of kinetic energy. It is always associated with the presence of a nucleus, which is necessary to conserve momentum in the process (Liverhant, 1960).

If the gamma ray photons of energy greater than 1.02 MeV may interact with the electric field around the nucleus then the process of pair production is possible. The probability of this interaction remains very low until the gamma ray energy approaches several MeV and therefore pair production is predominantly confined to high energy gamma rays. This interaction results in the complete absorption of the photon and the simultaneous creation of electron-positron pair. The production of these electron-positron pair represents the creation of matter from energy. The equivalence of matter and energy was set out by Einstein in quantitative form as \( E=mc^2 \). In order to create two electrons, a minimum energy of 1.02 MeV is necessary. Since the electrons are opposite in charge, no creation of charge is involved in pair production. If the energy of initiating photon \( h \) is greater than 1.02 MeV then the excess energy will appear as kinetic energy \( E \), shared between the electrons:

\[
hV = mc^2 + mc^2 + E^+ + E^- \quad (1.8)
\]

The positive electron does not have an isolated existence when at rest and when it comes to rest it combines with the neighbouring electrons. The two charges neutralize
each other and the mass of the two electrons is converted back into two photons of electromagnetic radiation, each of 0.51 MeV energy, travelling in opposite directions to each other. This is annihilation radiation. In practice this process is of little importance in the low atomic number except above about 20 MeV radiations. No simple expression exists for the probability of pair production per nucleus, but its magnitude varies as the square of the absorber atomic number (Knoll, 1989; Kapoor and Ramamurthy, 1986).

1.7. REVIEW OF RELEVANT LITERATURE

The radiation induced modifications is scientifically interesting, as well as practically important, because of its uniqueness and diverse applications range from geochronology and archeological dating to microchemical analysis and radiation dosimetry. The studies related to radiation effect in several solids have been accomplished using a broad range of different kinds of radiation such as gamma rays, X-rays, and UV-light, and also particle beams (electrons, protons, neutrons, ions, and ion-clusters).

Energetic charged particles on passing through the solids (dielectrics) lose their energy by excitation and ionization processes, and cause the radiation damage in materials along the path of the particle (Fleischer et al., 1965a). The material experiences physical and chemical changes within a cylindrical zone of typically several nanometers in diameter, along an ion trajectory. These are called latent ion tracks. An ion track consists of disordered material with broken chemical bonds and hence exhibits a higher chemical reactivity. These nuclear tracks in muscovite mica have been intensively studied by track etching experiments focusing on radiation damage for their scientific significance as well as their practical uses (Price and Walker, 1963; Fleischer et al., 1964a; Fleischer et al., 1964b; Huang and Walker, 1967; Fleischer et al., 1965b; Katz and Kobetich, 1968; Katcoff, 1969; Hashimoto et al., 1980; Dartyge et al., 1981; Khan, 1986; Snowden-Ifft and Chan, 1995).

Studies of the defects resulting from ion impact on many different materials, including mica, have been reported. Silk and Barnes (1959) observed tracks of the fission fragments in muscovite mica for the first time by spontaneous fission of a $^{238}$U nuclide using transmission electron microscopy. These tracks of the fission fragments
appeared as long and cylindrical damage zones together with lattice distortions. Subsequently, radiation damage in mica was performed using transmission electron microscopy by many authors (Bonfiglioli et al., 1961; Price and Walker, 1962). However, most investigations provided a typically track radius of a few nm (Lambert et al., 1970; Dartyge et al., 1976; Dartyge et al., 1981; Albrecht et al., 1985; Albrecht et al., 1986; Spohr et al., 1989; Singh and Singh, 1989; Vetter et al., 1998).

In 1991, the first image of Scanning Force Microscopy (SFM) of latent tracks in muscovite created after heavy ion irradiations was identified by Thibaudau et al. (1991). SFM studies on individual ion tracks in muscovite mica were carried out with a variety of imaging modes using different ion species (Bouffard et al., 1993; Toulemonde et al., 1994; Hagen et al., 1994; Daya et al., 1995a; Daya et al., 1995b; Daya et al., 1996; Ackermann et al., 1996; Neumann et al., 1996; Ackermann et al., 1998).

Eby et al. (1993) described the studies of muscovite mica surface bombarded with 600 keV Ar ions using CR-SFM. Snowden-Ifft and Chan (1995) studied etching properties of defects on mica surfaces bombarded by ions of $^{16}$O, $^{29}$Si, and $^{39}$K with a kinetic energy of keV/amu. Ruehlicke et al. (1995) reported that when mica was bombarded by highly charged (up to $q = 80+$) ions with a kinetic energy of 1.3 - 4.5 keV/amu, blister-like defects occurred. The ions used were Xe$^{1+}$; $^{35+}$; $^{44+}$; $^{50+}$, Kr$^{35+}$, U$^{70+}$, and Th$^{74+}$. No defects were found for mica bombarded by Xe$^{1+}$; $^{35+}$, but they observed a linearly increasing relationship between defect volume and incident charge for charges $q > 35+$. Bell et al. (1996) were also reported the results of a similar study using Xe ions of charge, states up to $q = 44+$ on materials like silicon, CR-39 polymer, and mica.

A track consists of an inner amorphous core and a surrounding zone, in which the lattice is disturbed but not destroyed, resolved using Wide-angle X-ray scattering experiments on powdered mica (Chailley et al., 1994; Chailley et al., 1996). The radiation damage was also studied corresponding to muscovite by means of track etching, partially with the aim of dating the mineral (Price and Walker, 1963; Huang and Walker, 1967; Templier et al., 1996; Glasmacher et al., 2003; Gogen and Wagner, 2000; Lang et al., 2002a; Lang et al., 2003; Bernaola and Martin, 2005).
Studies regarding the impact of ion irradiation on phlogopite mica have been reported but are rather limited. Wang et al., (1998) irradiated four different mica compositions, i.e. muscovite, phlogopite, biotite and lepidolite with 1.5 MeV Kr ions in the temperature range between 20 and 1023 K and characterized by in situ and high resolution transmission electron microscopy (TEM). Hashemi-Nezhad (1997; 1998) studied the morphology of different types of etched fission tracks (triangular, polygonal or hexagonal) in phlogopite mica and also suggested that an energy loss dE/dx smaller than about 9 keV/nm leads to triangular etch pits. Lang et al. (2002a; 2002b) reported that when phlogopite mica was bombarded with ions, hillock defects occurred and were investigated using SFM. Etching behaviour of alpha-recoil tracks in natural dark mica studied via artificial ion tracks observed by Lang et al. (2003). Lang et al. (2004) studied etching properties of defects on phlogopite mica surfaces bombarded by ions of $^{58}$Ni with a kinetic energy of 81MeV and observed triangular tracks with energy loss below 5.7 keV/nm and hexagonal above 8.8 keV/nm. Hashmi-Nezhad (2005) observed that the etched track contour geometry in phlogopite mica depends on the extent of the radiation damage present in the track core. Jonckheere et al. (2005) reported occurrences of fission-track, recoil-track and dislocation etch pits in tri-octahedral phlogopite and di-octahedral muscovite.

High-energy ion tracks (374 MeV Au$^{26+}$) in thin films (mica) were examined with transmission electron microscopy to investigate nanopore formation (Follstaedt et al., 2006). Singh et al. (2010a) investigated morphological studies of heavy ions irradiated mica. Nowadays, these minerals irradiated with different heavy ions are used in nanotechnology as a template (Mo et al., 2012) for the formation of nanostructure (Aumayr et al., 2008; Ritter et al., 2010), nanowires and nanodots (Wang et al., 2012). Zhou et al. (2013) irradiate muscovite with lithium, carbon and oxygen ions and hillock-like structure on the mica surface was observed using AFM. Nanoscale hillocks produced by swift and heavy $^{129}$Iodine ions with variable energies in the MeV range on the surface of mica, apatite and zircon been evaluated by the means of Atomic Force Microscopy (AFM) (Kohlmann et al., 2013).

Various types of radiation-induced defects have been identified in several clay minerals (Pushkareva, 2002; Fourdrin et al., 2009; Allard and Calas, 2009; Allard et al.,
Nagabhushana et al. (2012) investigated Ionoluminescence properties of natural kyanite mineral collected from different parts of India. Sakharov et al. (2001) studied unusual X-ray characteristics of vermiculite from wiry, lower Silesia, Poland. A good amount of work has been done on the effect of microwaves on exfoliation properties and thermal behaviour of vermiculite by several groups (Marcos et al., 2009; Muiambo et al., 2010; Marcos et al., 2011; Folorunso et al., 2012). Campos et al. (2009) characterized natural mineral vermiculite from Santa Marta-Colombia by several techniques. Literature survey, on the other hand, revealed no work on gamma and heavy ion irradiated induced modifications of vermiculite.

Little information is available on the optical, chemical, structural, and dielectric properties of these minerals without irradiation. Popper (1951) calculated the absorption coefficient in Congo green, Rhodesian ruby and synthetic mica and found that synthetic mica has lower absorption as compared to Congo green and Rhodesian ruby mica. Grum-Grzhimails et al. (1958) observed absorption spectra in Russian muscovite and phlogopite micas. Dhar and Das (1966) observed the transmission curves of Indian mica obtained from Bihar, Madras and Rajasthan. Davidson and Vickers (1972) measured optical properties of mica in the vacuum ultraviolet, Le calvez (1968) calculated reflectivity of muscovite between 400- 2800Å. Karickhoff and Bailey (1973) studied optical absorption spectra of clay minerals and reveals the utility of this spectroscopy in the elucidation of structural, physical, and chemical properties of such systems. To the best of our knowledge, there has been no published work on the optical properties of irradiated natural phyllosilicate minerals.

The study of the dielectric properties of minerals is very informative because of their applications in insulation industry, electrical engineering, opto-electric devices and other fields of science and technology. Rosenholtz and Smith (1936) calculated the dielectric constant of various mineral powders. Davidson and Yoffe (1965) investigated the dielectric breakdown in thin mica crystals. Ashida et al. (1966) reported the influence of thermal treatment on the electric conductivity of muscovite mica. Gudhov and Metsik (1973) reported the relative permittivity and loss tangent of natural muscovite and phlogopite at high frequencies (3 to 36.8 GHz). Olhoeft (1976) studied
the electrical properties of rocks. Chaudhry et al. (1985) established the dielectric properties of muscovite mica in frequency range (0.01 Hz to 100 kHz) and in the temperature range between 173 K and 368 K. Chaudhry and Jonscher, (1985) observed dielectric properties of mica paper in the frequency range (10^2 to 10^4 Hz) and found that complex capacitance of mica paper is influenced exponentially by variation in reciprocal of temperature (314K to 914K) and relative humidity (Chaudhry and Jonscher, 1985; Bano and Jonscher, 1992). Measurements of the dielectric properties of mica were reported with platinum, silver and graphite electrodes in the frequency range 0.01 to 10000 Hz at fixed temperatures in the range up to 956 K (Chaudhry and Jonscher, 1988). Dielectric response of wet muscovite mica was measured as a function of frequency in the range 10 mHz-10 kHz and humidity in the range 0% - 97% (Chaudhry, 1992). The dielectric response of mica-type silicates and layered double hydroxides were studied in the frequency range 10 Hz – 100 MHz (Mehrotra and Giannelis, 1992). Ruscher and Gall (1997) investigated the dielectric properties of biotite and vermiculite at variable frequencies (0.1 to 1000 kHz) and as a function of temperature (300 K - 900 K). Dawy (2002) have done work in the heated mica sheets in the frequency range (0.1-100 kHz) using AG-4311B RCL meter. They found that the dielectric constant and dielectric loss were nearly stable till 600°C but showing an increase at 800 °C and 900°C. Studies regarding dielectric properties as a function of temperature have been carried out by number of authors (Dye and Hartshor, 1924; Callinam, 1952; Howell and Licastro, 1961; Singh et al., 2011; Kaur et al., 2012). No literature is found on the modifying effect of ionizing radiation on dielectric properties of phyllosilicate minerals.

Vibrational infrared spectroscopy is one of the most useful experimental techniques available for understanding irradiation effects on structural studies. Serratosa and Bradley (1958) observed that the efficiency of absorption in the frequencies associated with OH bond is a function of the angle between the bond axis and the plane of the electric vector of the light. Infra red absorption spectra for tetrahedral aluminium in different types of mica were studied by Lyon and Tuddenham (1960). Effect of heating on Infra-red spectra of Siberian mica was investigated by Metsik and Shishelova (1971). Shishelova et al. (1974) observed changes in the infrared spectra of

Thermo luminescence (TL) is an important phenomenon that takes place in various irradiated natural minerals. McDougall (1968) observed natural thermoluminescence of igneous rocks and associated ore deposits. Nishita et al. (1974) have reported two peaks of Muscovite mica at 220 °C and 350 °C. Mukhlya et al. (1977) have showed stage of mineralization from thermoluminescent properties of Muscovite. Kristianpoller et al. (1988) have studied natural and beta induced TL properties of muscovite at linear heating rate of 5 °C/s. Kasuya et al. (1989) studied the annealing effects on the sensitivity of gamma induced thermoluminescence in lepidolite mica. Barcena et al. (1999) have investigated TL properties in muscovite, sericite and phlogopite irradiated with gamma and beta rays. Ige et al. (2006) have studied TL response of muscovite samples from south-western Nigeria and observed two peaks around 238 °C and 330 °C. Soliman and Aziz in 2008 reported the gamma and electron dose responses in synthetic muscovite mica. Singh et al. (2012) studied the thermoluminescence characteristics of muscovite mica collected from nilore mica belt in India. The TL glow curves of X-ray irradiated micrograin natural muscovite mica were recorded within 298-520 K at various linear heating rates (Kalita and Wary, 2014). However, the effect of gamma radiation at high doses and heavy ions on TL properties has not been investigated so far. Such knowledge is particularly useful for the proposed application of glow curves for archaeological dating. In the present research work, it is proposed to investigate the thermo luminescence response of gamma and heavy ion irradiated natural phyllosilicate minerals (phlogopite, muscovite and vermiculite) to study their relevance to dating and dosimetry.

Although some work on the study of optical, infrared, structural, dielectric and thermoluminescence properties of phyllosilicate minerals is available in literature, but the effect of ionizing radiation on these properties have not been investigated so far. Therefore, in the present work, the research investigations on the effect of gamma and swift heavy ions on optical, chemical, structural, dielectric and thermoluminescence properties of some phyllosilicate minerals are carried out to identify and characterize
radiation induced defects in phyllosilicate minerals and application in radiation dosimetry.

1.8. MOTIVATION FOR THE PRESENT WORK

Phyllosilicates are invaluable in electrical industry applications because of its unique combination of physical, chemical, thermal, mechanical, irradiation (sensitive for radiation detection, used for dosimetry purpose) and dielectric (great dielectric strength, Uniform dielectric constant, capacitance stability, low power loss) properties. Radiation induced amorphization may affect the stability of materials, resulting in significant changes of important physical, chemical, structural, dielectric and thermoluminescence properties which in turns leads them to many applications.

After an extensive study of literature of irradiation effects on the minerals, it has been found that though the effects of heavy ion irradiation on these minerals have been investigated by many researchers regarding the changes in morphological and etching properties of mica mineral. The effects of gamma and heavy ion irradiation on the optical parameters (like band gap energy and Urbach energy), dielectric parameters (such as dielectric constant, dielectric loss, and ac conductivity), structural parameters (like crystallite size, microstrain, dislocation density) have not been reported in details. The literature shows that study is restricted only to the morphological, annealing and etching properties. However, meager information of the thermoluminescence (TL) behaviour of phyllosilicate minerals under different type of radiations is found in literature. Thus there is a need to carry out such types of investigations.

In this thesis work, the emphasis is given on the behaviour of optical, structural, chemical and dielectric properties of natural phyllosilicate minerals under different types of ionizing radiations. Attempts have been made to understand the TL behaviour of natural Indian phyllosilicate minerals to explore their potency for magnificent applications in radiation dosimetry.

1.9. AIMS AND OBJECTIVES OF THE THESIS

The present problem focuses on the study of dielectric, optical, structural, chemical and thermoluminescence properties of phyllosilicate minerals and to explore
the effect of gamma radiation and heavy ion beam on these properties. The phyllosilicate minerals chosen for the present study are phlogopite, muscovite and vermiculite minerals. The research objectives of the present work follow:

- To examine the optical, dielectric, structural and chemical properties of natural phyllosilicate (phlogopite, muscovite and vermiculite) minerals.
- To expose phyllosilicate minerals to gamma radiation ranges from kilo Gray to mega Gray.
- To irradiate the phyllosilicate minerals with swift heavy ions at different fluences.
- To study the influence of gamma and swift heavy ion irradiation on dielectric properties such as dielectric constant, dielectric loss and ac conductivity to identify good materials which have high thermal insulation property and radiation shielding capacity.
- To analyse the structural and chemical properties of phyllosilicate minerals for identification and characterization of defects and understanding their use in radiation dosimetry.
- To investigate the optical properties of gamma and heavy ion irradiated phyllosilicate minerals for understanding the use of these minerals in optical applications.
- To examine the thermoluminescence response of gamma and heavy ion irradiated natural phyllosilicate minerals to study their significance in TL dating and radiation dosimetry.