CHAPTER I

INTRODUCTION

1. Introduction

1.1. Radiation Effects on Matter

1.1.1. General

The discoveries of X-rays and radioactivity lead to the conclusion that energetic radiations are capable of inducing physical, chemical and biochemical transformations in matter. The effects of irradiation (i.e., absorption of radiation) depend upon composition of matter, nature and amount of incident radiation. All elementary particles, both charged and uncharged having energies greater than 100 eV are referred to as nuclear radiation. Since the lower energy limit is very high when compared to ionization energies (usually <15eV) and chemical bond energies (normally 1-5eV) nuclear radiation causes ionization during its passage through matter and hence the common name, ionizing radiation. The passage of such radiation through matter results in energy transfer to the atoms and molecules comprising the absorbed material until the average kinetic energy of the
impinching particle of radiation reaches that of the atoms in the material i.e., until thermal equilibrium is attained. This energy transfer results initially in excitation and ionization in the absorbing material leading to physical and chemical changes. The study of these effects is the domain of radiation chemistry.

1.1.2. Interaction of gamma radiation with matter

Depending upon the amount of energy absorbed, the principal modes of interaction of \( \gamma \)-ray with matter are (1) photoelectric effect (2) Compton scattering (3) pair production and (4) nuclear reaction. Of these, photoelectric effect is the dominant mode of interaction for lower energy (<0.1 MeV), Compton scattering for low and medium energy (0.1 to 10 MeV) and for energies greater than 10 MeV pair production. Nuclear reactions are important for very high energies only. Excluding nuclear reactions, in all three processes electrons are ejected which causes the internal bombardment of the target (i.e., absorbed material) by energetic electrons. The effects of \( \gamma \)-radiation are therefore exclusively due to secondary electrons which produce ionization and excitation of atoms or molecules in the target. Depending upon the physical state, crystalline nature, molecular structure etc. of the target, different consequences are possible.

1.1.2.1. Chemical consequences of excitation and ionization

In crystalline solids as a result of ionization lattice vacancies are created. Ionization results in simple trapping of electrons and production of
electron holes. Thus crystal defects are introduced which increase the energy content of the crystal and subsequent chemical damage. In ionic solids with polyatomic ions e.g. NO$_3^-$, ClO$_4^-$ etc., the important consequence of electronic excitation is bond rupture leading to chemical damage. Thus production of damage, displacements and extended lattice defects are the predominant effects of irradiation in molecular ions.$^{1-3}$ These effects lead to changes in physical and chemical properties.

1.1.2.2. Generation sources

The sources for generation of radiolytic products in solids$^{4-6}$ include isotope sources, nuclear reactions and particle accelerators. Natural as well as artificial radioactive isotopes have been used as generator of radiation products e.g. $^{210}$Po, $^{137}$Cs, and $^{60}$Co for radiolytic purposes$^{4-7}$. The X-ray machine, cyclotron, van de Graaff accelerator and linear electron accelerator have been employed most frequently for radiation-chemical studies$^8$. The most commonly used $\gamma$-ray sources are $^{60}$Co and electron beam accelerators.

1.1.2.3. Detection and identification of radiolytic products

The radiation induced decomposition of several crystalline inorganic compounds containing oxyanions like nitrates, halates, carboxylates etc., have been studied. Information about structure and identities of primary ionic species has been obtained from mass spectrometry, photoelectric and vacuum ultra violet spectroscopy. ESR techniques have been extensively used in the study of free radicals. ESR studies of gamma irradiated Li$_2$CO$_3$ and CaSO$_4$
detected the presence of \( \text{CO}_3^- \), \( \text{CO}_2^- \), \( \text{SO}_4^- \) and \( \text{SO}_3^- \) as radiolytic products.\(^9\) Gamma radiolytic decomposition of sodium and potassium nitrates detected the presence of \( \text{NO}_3^- \) and \( \text{NO}_2^- \) as radiation damage products.\(^10\) ESR studies of gamma ray induced decomposition of lanthanum, europium and terbium nitrates suggest the formation of radical species which may interact with the radical species of nitrate (\( \text{NO}_3^- \), \( \text{NO}_2^- \) etc.) causing enhanced decomposition by energy transfer.\(^11\) ESR study of lithium nitrate irradiated with gamma ray detected \( \text{NO}_2 \), \( \text{NO}_3 \) radicals and \( \text{NO}_2^- \), \( \text{NO}_3^- \) and \( \text{O}_2^- \) ionic radicals.\(^12\) Room temperature EPR spectrum of gamma irradiated europium doped yttrium borate\(^13\) revealed the formation of two hole trapped radicals namely \( \text{BO}_3^- \) and \( \text{O}_2^- \). The presence of CHCH\(_2\) radical and CH\(_3\) and CHCH\(_2\)CH\(_2\)CH\(_2\) radicals are detected by the ESR studies of gamma irradiated single crystals of cholesteryl acetate and cholesteryl chloroformate.\(^14\) Much insight into radiation process and radiation induced radical reaction has been gained by means of pulse radiolysis method. Techniques used to follow the transient behaviour of short lived radiolytic species are absorption spectroscopy, ESR, conductivity and polarography.

1.1.2.4. Mechanism of radiolytic decomposition of inorganic solids

**Nitrate**

The radiolytic fragments are \( \text{NO}_2^- \), \( \text{O}_2^- \), (\( \text{NO}_2^- \)), (\( \text{NO}_3^- \)), \( \text{NO}_3 \), \( \text{O}_2^- \), \( \text{NO}_2^2^- \), \( \text{NO}_3^2^- \), \( \text{O}_3^-\text{O}_4^-\text{O}_2^2^- \), \( \text{N}_2\text{O}_3^2^- \) and \( \text{N}_2\text{O}_4 \) and \( \text{NO}_2 \).\(^{15-34}\) The possible effect of radiation on nitrate may be schematically shown as below.
Ionization and excitation.

\[ \text{NO}_3^- \rightarrow \text{NO}_3, \text{NO}_3^* \] (1.1)
\[ \text{NO}_3 \rightarrow \text{NO}_2 + \text{O} \] (1.2)

The primary dissociation events are

\[ \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 \] (1.3)
\[ \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O} \] (1.4)
\[ \text{NO}_3^* \rightarrow \text{NO} + \text{O}_2^- \] (1.5)

Electron capture

\[ \rightarrow (\text{NO}_3^-)^-, (\text{NO}_2^-)^- \] (1.6)

A different scheme has also been proposed,

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O} \] (1.7)

The oxygen fragment reacting as

\[ \text{NO}_2^- + \text{O} \rightarrow \text{NO}_3^- \] (1.8)
\[ \text{NO}_3^- + \text{O} \rightarrow \text{NO}_2^- + \text{O}_2 \] (1.9)

and also

\[ \text{O} + \text{O} \rightarrow \text{O}_2 \] (1.10)

According to Cunningham\textsuperscript{25,26} the primary fragments in low temperature irradiation of crystalline nitrates are NO and O\textsubscript{2}^-.

\[ \text{NO}_3^- \rightarrow \text{NO} + \text{O}_2^- \] (1.11)

When crystals are irradiated at room temperature or above, the primary radical species back react to produce NO\textsubscript{2}^- and O.

\[ \text{NO} + \text{O}_2^- \leftrightarrow \text{NO}_3^* \leftrightarrow \text{NO}_2^- + \text{O} \] (1.12)
1.1.2.5. Applications

The subject of radiation effects in solids is an important one, a subject of worldwide attention in modern day science and engineering curricula. Specifically radiation damage is one of the most novel and proficient means to produce metastable phases of solid materials with new and unusual properties that in turn can be exploited in technological applications. Knowledge regarding radiation damage defects also benefits the development of advanced materials. The effect of γ-ray and ionizing radiations on the physicochemical, surface and catalytic properties, lattice defects, structure and thermal stability of various solids have been investigated.\textsuperscript{35-37} Gamma irradiation has been successfully employed for the synthesis of nanoparticles\textsuperscript{38,39} and semiconductors.\textsuperscript{40,41} As irradiation leads to excitation and ionization of molecules in all materials, the excited species decompose to yield highly reactive free radicals in vast majority of systems. These are precursors of further reaction such as oxidation, reduction, polymerization, cross-linking etc., thus finding applications in various industrial processes.

The biological applications include conservation of food,\textsuperscript{42-44} sterilization of medical devices\textsuperscript{45,46}, radiation therapy\textsuperscript{47,48}, eradication of insects\textsuperscript{49,50} etc.
1.2. Thermal Studies

1.2.1. Thermal decomposition of crystalline solids and role of defects thereon

The solid decomposition can be described in terms of a general hypothesis that the reaction consists of the formation of nuclei and their subsequent growth. The process of nucleation occurs when the fluctuations of the local energy of the crystals are sufficient to provide the necessary activation energy for the formation of a nucleus. Potential nucleus forming sites are generally associated with lattice imperfections. Thus imperfect regions of lattice possess higher reactivity. As irradiation generates crystal defects the number as well as growth of potential nucleus forming sites is increased thereby enhancing the decomposition reactivity. A search of the available literature revealed that the thermal process is enhanced upon irradiation in most cases with a few exceptions where the reverse is true. It is established that the kinetics of thermal decomposition is considerably affected by pre-exposure to ionizing radiation.

1.2.2. Review of earlier studies

Reported investigations are classified according to the respective thermoanalytic techniques employed.

(1) Gas evolution method in which thermal decomposition is followed at each temperature by measuring the pressure of the gas evolved at different times on heating.
(2) Isothermal or static thermogravimetry in which the sample weight is recorded as a function of time at constant temperature.

(3) Non-isothermal or dynamic thermogravimetry in which the sample is heated in an environment whose temperature is changing in a pre-determined manner, generally at a linear rate. Sample mass is recorded as a function of temperature.

1.2.2.1. Effect of irradiation on thermal decomposition of inorganic salts

Thermal decomposition studies of γ-irradiated sodium bromate, potassium bromate, barium bromate, calcium bromate, lead bromate and cadmium bromate by gas evolution method have been reported. The kinetics of thermal decomposition of irradiated potassium bromate and caesium bromate were found to be similar. The effect of γ-radiation on thermal decomposition of lead nitrate and strontium nitrate has been studied by the gas evolution method. The decomposition occurs in four stages in both cases. Irradiation enhances the rate of decomposition of strontium nitrate without altering the mechanism of the process, the effect being higher at higher doses.

Thermal decomposition of oxalates of silver, lead, nickel, uranium, thorium, barium, samarium, yttrium, barium titanyloxalate and hydrated barium oxalate has been studied by gas evolution method. Irradiation increases the energy of activation of the decay stage without affecting the same in the acceleratory period. In hydrated barium oxalate, irradiation enhances thermal decomposition and analysis of data reveals that
the two dimensional phase boundary reaction model gives the best fit to the results. In yttrium and samarium oxalates, the fractional decomposition $\alpha$ is enhanced by irradiation, the effect being higher at higher doses in both cases. Irradiation has marginal effect on the energy of activation of the acceleratory and decay periods in samarium oxalate but it reduces the same in the former stage and reverse phenomenon occurs in the latter period in the case of yttrium oxalate. The effect of $\gamma$-radiation on thermal decomposition of a mixture of barium oxalate and copper oxide, yttrium oxalate and copper oxide studied by gas evolution method is also reported. It is seen that irradiation enhances decomposition rate and diminishes the activation energy in both cases.

The effect of $\gamma$-radiation on the thermal decomposition of various acetates, carbonates, oxalates, permanganates etc. has been studied by isothermal thermogravimetric method. It is observed that irradiation retards the thermal process in the case of cobalt acetate and gadolinium acetate and enhances the same in uranyl acetate, samarium acetate and thallous acetate. In dysprosium acetate irradiation was observed to enhance the rate of decomposition without modifying the mechanism of the thermal decomposition. The isothermal decomposition of unirradiated and $\gamma$-irradiated zinc and palladium acetates has been studied. The results showed that the activation energies of the main decomposition process were lowered upon irradiation.
Isothermal thermogravimetric studies of irradiated nickel oxalate and potassium nickel oxalate\textsuperscript{82-83} have also been reported. Pre-irradiation changed the kinetics of propagation and growth of the decomposition centers in highly irradiated samples of nickel oxalate attributed to radiation damage of the crystal. Gamma irradiation decreased the thermal stability of Co\textsubscript{3}O\textsubscript{4} to an extent proportional to the dose employed. On the other hand, this treatment increased the thermal stability of both CuO and Cu\textsubscript{2}O.\textsuperscript{84} Effect of gamma radiation on silver oxide has been studied and it is seen that irradiation has no effect on thermal decomposition.\textsuperscript{85}

The thermogravimetric studies (under non-isothermal conditions) of bromates, chlorates, nitrates, acetates, oxalates, permanganates etc. have been reported. The thermal decomposition studies of γ-irradiated potassium bromate\textsuperscript{86} show that the rate controlling process is a phase boundary assuming cylindrical symmetry. The analysis of thermoanalytical data of magnesium calcium bromate\textsuperscript{88}, strontium bromate\textsuperscript{89} and zinc bromate\textsuperscript{90} reveals that the rate controlling process is a phase boundary assuming spherical symmetry. It is seen that as irradiation dose increases activation energy decreases.

The thermal decomposition of γ-irradiated potassium chlorate\textsuperscript{91} has been studied by dynamic thermogravimetry. Irradiation enhances the decomposition and the effect increases with the irradiation dose. The thermal decomposition of silver cyanamide\textsuperscript{92} irradiated with γ-rays, thermal neutrons
and fission fragments has been reported. Irradiation with $\gamma$-rays has no effect on thermal decomposition of the salt. Neutron irradiation causes acceleration in the decomposition of the crystalline substance while in the case of powder material no effect on thermal decomposition is observed.

Non-isothermal studies of strontium nitrate$^{93,94}$, lead nitrate$^{95}$, and cadmium nitrate$^{96}$ have been reported. It is seen that irradiation enhances thermal decomposition and the activation energy is lowered. The enhancement of the decomposition may be attributed to the damage $\text{NO}_2^-$ which catalyses the reaction. The thermal decomposition of gamma irradiated anhydrous lanthanum nitrate was studied by dynamic thermogravimetry.$^{97}$ The decomposition proceeds via three consecutive stages characterized by different activation energies. The activation energies of all the three stages decrease on irradiation.

Influence of $\gamma$-irradiation on the decomposition of barium oxalate$^{98}$, lanthanum-barium oxalate$^{99}$, calcium-gadolinium oxalate$^{100}$, zinc oxalate$^{101}$, manganese oxalate$^{102}$ etc. have been studied. Analysis of the thermoanalytical data of zinc oxalate and manganese oxalate revealed that irradiation lowers $E$, $A$ and $\Delta S$ values for zinc oxalate while in the case of manganese oxalate these values reached a minimum and then increased. The effect of gamma radiation on thermal decomposition of ammonium oxalate monohydrate has been studied by dynamic thermogravimetry.$^{103}$ Kinetic analysis of thermo-analytical data revealed that activation energy for the dehydration step is much
higher than that in the non-irradiated sample. The activation energy for the decomposition step is lowered to a small extent, but does not show regular variation.

The thermal decomposition of γ-ray or neutron irradiated ammonium perchlorate has been studied in detail. Thermogravimetric study on ammonium perchlorate irradiated with γ-ray or neutrons show that if irradiation doses are less than $10^9$ eV/g the decomposition rate decreases abruptly after the transition point is reached. At doses of $10^{20}$ eV/g decomposition starts before reaching the transition point (around 508 K). Effect of γ-radiation on the thermal decomposition of barium perchlorate has been reported. Prout and Boldyrev has reported that the rate of thermal decomposition is enhanced in all permanganates upon irradiation.

1.2.2.2. Effect of irradiation on thermal decomposition of complexes.

The effect of γ-radiation on the thermal decomposition kinetics of a few metal complexes has been studied. The isothermal decomposition kinetics of γ-irradiated $[\text{Co(NH}_3\text{)}_6\text{]}\text{Cl}_3$ has been studied. It is seen that pre-treatment reduced the length of the induction period and increased the rate of decomposition. The activation energy is reduced from 46.82 to 20.22 kJ mol$^{-1}$ upon pre-irradiation.

The kinetics of isothermal decomposition of cobalt(II)malonato complex, both irradiated and unirradiated has been investigated.
activation energy for the dehydration stage was found to be decreased upon irradiation while the same for the decomposition stage remained unaltered.

The isothermal decomposition kinetics of $\gamma$-irradiated cobalt(II) succinate complexes has also been reported. Irradiation enhances both the decomposition and dehydration reaction without modifying their mechanism. The activation energy was found to decrease with increasing irradiation dose.

Thermal behaviour of a series of mixed ligand complexes of the formula $[\text{Co(tyr)(gly)H}_2\text{O}]_2, [\text{Co(tyr)(ala)H}_2\text{O}]_2, [\text{Co(tyr)(thr)H}_2\text{O}]_2$, where tyr = L tyrosine, gly = glycine, ala = alanine and thr = threonine have been studied before and after $\gamma$-irradiation.

Mixed ligand complexes of the type $[\text{M(X-QA)}(\text{aa})]$ and $[\text{Ni(X-QA)}_2(\text{Haa})(\text{H}_2\text{O})]$ where X-HQA = 5 arylazo-8-hydroxy quinoline derivatives, M = Co(II) or Cu(II) and Haa = glycine, alanine or methionine have been prepared and characterized. The thermal behaviour of the complexes has been studied before and after $\gamma$-irradiation. The irradiated samples exhibit essentially the same TG profile compared to those before irradiation. Irradiation enhances thermal decomposition lowering thermal and kinetic parameters. Co(II) and Cu(II) complexes display a greater decrease in activation energy than those of the Ni(II) complexes.

Effect of $\gamma$-radiation on non-isothermal decomposition kinetics of bis(diethylenetriamine) cobalt(II) nitrate and bis(diethylenetriamine) zinc(II)
nitrate have been studied in nitrogen atmosphere at a heating rate of 10°C/minute. The data were analyzed by Coats-Redfern, Freeman-Caroll and Horowitz-Metzger methods. The results showed that irradiation enhanced thermal decomposition in both the complexes. Activation energy and associated kinetic parameters are lowered upon irradiation and the extent of lowering is higher in cobalt complex compared to zinc complex.\textsuperscript{122}

The effect of varying doses of gamma irradiation (25 kGy, 50 kGy and 75 kGy) on Co(II), Ni(II) and Zn(II) complexes of diethylenetriamine has been investigated.\textsuperscript{123} The activation energy for the deamination stage decreases remarkably upon irradiation in the case of cobalt complex, markedly increases upon irradiation for nickel complex and then decreases regularly to a very high extent. In zinc complex the activation energy decreases upon irradiation but this decrease is small. Since the ligand is the same, apart from the damage fragments of ligand, another factor may also be involved in the enhancement of deamination. Cobalt(II) and nickel(II) have crystal field stabilization energies in an octahedral environment, but zinc has no CFSE. It is possible that irradiation results in a decrease of CFSE so that deamination is faster, consequently the activation energy decreases. The initial increase in activation energy for nickel complex may be due to the involvement of radiolytic fragments of lattice water. As irradiation dose increases the activation energy decreases regularly.
1.2.3 Summary of effect of radiation on thermal decomposition

Solid state reactivity can be altered by pre-exposure to energetic radiations. The observed general effects of irradiation on thermal decomposition of solids include abbreviation of the induction period and enhancement of rate constants for both acceleratory and decay stages of reaction. Exceptions are also reported in which irradiation retard the thermal process and inhibit the decomposition due to the formation of long lived trapped radicals and holes in the host lattice.

1.3. X-ray Diffraction Studies

1.3.1. General

Lattice imperfections caused by irradiation influence the X-ray diffraction pattern of a substance. The quantity and structure of a new phase which accumulate during radiolysis and also the accompanying changes in the degree of imperfection of the crystal can be studied by X-ray and electron diffraction methods. In crystalline solids irradiation generates lattice vacancies causing an ion or atom to occupy a non-equilibrium interstitial position. Further the localized dissipation of energy can result in lattice oscillations, terminating in some reorientation of the local regions in the crystal lattice. The presence of defects in a crystalline lattice may change both the unit cell size and the physical size of the crystal resulting in lattice distortion.
1.3.2. Brief review on XRD studies of irradiated materials.

The effects of gamma radiation on few crystals have been investigated. X-ray diffraction powder pattern of zinc acetate has been studied before and after gamma irradiation.\textsuperscript{80} XRD measurements showed that $\gamma$-irradiation induced significant changes in the crystalline identity of zinc acetate. The changes in crystal structure of palladium acetate\textsuperscript{81}, cobaltous acetate\textsuperscript{126} and neodymium acetate\textsuperscript{127} upon irradiation have been studied. High damage is induced by $\gamma$-irradiation on the X-ray diffraction pattern.

The effects of $\gamma$-radiation upon the characteristic X-ray diffraction and thermal decomposition of MnCO$_3$ were investigated.\textsuperscript{128} The results obtained revealed that the employed doses of $\gamma$-radiation brought about a two-fold increase in the relative intensity of the main diffraction line of MnCO$_3$($d = 2.85\text{Å}$) indicating an enhanced increase in the crystallinity of the MnCO$_3$ phase. No broadening in the diffraction lines of MnCO$_3$ was observed in the case of irradiated solids indicating the absence of any change in the lattice parameter of $\gamma$-irradiated manganese carbonate sample. XRD studies of CaCO$_3$ in egg shell\textsuperscript{129} have been carried out before and after gamma irradiation. Formation of nanodefects in LiF crystals under gamma irradiation has been studied.\textsuperscript{130}

Transformations on the alkali-halide crystal surface by the high energy irradiation such as X-ray, UV-radiation, gamma-radiation and cold air plasma have been investigated\textsuperscript{131}. The interaction on the solid-gaseous
interphase results in a lamina being formed on the crystal surface. The lamina usually includes such compounds as $\text{MeNO}_3$, $\text{MeNO}_2$, $\text{MeXO}_3$, $\text{MeXO}_4$ where Me is the alkali crystal, X is the halide. It has been set up by the methods of electronic microscopy and X-ray diffraction analysis that the compounds formed crystallize into islets at the initial steps.

XRD studies of irradiated nitrates have been carried out. Natural non-pretreated poly crystalline lithium nitrate was irradiated by gamma rays of $^{60}\text{Co}$ with total radiation doses from 10 to 100 Mrad, at room temperature.\textsuperscript{12} No colour centers were observed in samples irradiated in this range. X-ray studies evidenced the distortion of the lattice planes. $\gamma$-pyrolysis of aluminium nitrate nonahydrate have been investigated by means of X-ray diffraction studies\textsuperscript{132}. Gamma ray induced decompositions of $\text{NaNO}_3$ with 0.1-99.9 mol % $\text{KNO}_3$ and $\text{Sr(NO}_3)_2$ with 0.1-99.9 mol % of $\text{Ba(NO}_3)_2$ have been studied in the dose range of 60-500kGy. XRD patterns suggest the possibility of microcrystalline phase changes after $\gamma$-irradiation.\textsuperscript{133} Gamma radiolysis of solid zirconium nitrate and its binary mixtures with potassium halides\textsuperscript{9} have been carried out by XRD patterns.\textsuperscript{134}

Effects of gamma radiation on physicochemical state of surface and catalytic properties of CuO/MgO and NiO/MgO systems were investigated.\textsuperscript{135} XRD studies revealed that $\gamma$-irradiation upto 0.8 Mgy of CuO/MgO system at 450°C effected a measurable decrease in the crystallite size of CuO phase with subsequent increase in its degree of ordering. Gamma irradiation of
NiO/MgO system at 450°C solids upto 0.8 MGy increased the degree of ordering of MgO and NiO phases without changing their crystallite size. The effects of γ-radiation on the particle size, specific surface area and catalytic activity of CO₃O₄ and NiO solids were investigated. The results showed that γ-irradiation resulted in a small decrease in the particle size of the investigated solids and effected a progressive increase in their specific surface areas.

Pure Na₂S₂O₃ 5H₂O was investigated for its X-ray diffraction before and after various gamma ray absorbed doses. X-ray diffraction pattern shows that sodium thiosulphate suffers phase transformation and increased degree of crystallinity. During the irradiation, the material continues to undergo phase transformation. This may be due to the fact that γ-irradiation appears to enhance the crystal growth rate without increasing the number of potential nuclei.

Structural stability of the plasma sprayed alumina has been studied after its exposure to fast-neutrons and gamma irradiation. The fast neutron fluence (E>0.1 MeV) was 1.8×10²² nm⁻². As shown by X-ray diffraction and high resolution transmission electron microscopy the microstructure of alumina consisted of crystalline regions and regions which underwent considerable disordering during plasma spray deposition. This microstructure has been basically preserved during irradiation. The light brown appearance of the irradiated alumina indicated the formation of isolated point defects.
The accompanying near-isotropic swelling resulted in a small increase in lattice spacing as measured by X-ray diffraction.

The influence of gamma radiation on multilayer Al Ga As/In Ga As/ Ga As transistor heterostructures has been studied by X-ray diffraction analysis and transmission electron microscopy. It was found that irradiation with doses exceeding $3 \times 10^7$ rad leads to destruction of the Ga As layer on the surface of these structures. Dislocations are formed in the cap layer of the structure and composition of the thin In Ga As channel layer occur at doses lower than $10^8$ rad.

The effect of $\gamma$-irradiation on the structural and electrical properties of rare earth ferrite, $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Ce}_y\text{Fe}_{2-y}\text{O}_4$ has been investigated. XRD of unirradiated and irradiated samples showed the formation of cubic spinel structure. Long term irradiation effects on gamma irradiated Nylon 6, 12 fibres, irradiated six years ago, have been determined. Changes in the shape and size of the crystals (crystallinity degree) are studied. The crystallite size increases with storage time. The influence of gamma irradiation on GeSe films has been studied by XRD techniques. The high energy irradiation has been shown to stimulate structural transformations and to produce changes in the electron-defect subsystem of the films. XRD patterns of ethylene vinyl-acetate co-polymer rubber /magnesium hydroxide blend cross linked by $^{60}\text{Co}$ irradiation in the presence of trimethylolpropanetriacrylate has been investigated. Gamma irradiated polyethylene films has been characterized.
by X-ray diffraction. Parameters of X-ray diffraction such as number of
diffraction patterns, peak position and width of diffraction pattern have been
studied.

Microstructure of irradiated zirconium-based alloys has been
characterized by X-ray diffraction line profile analysis.\textsuperscript{145} Alloys have been
irradiated with 11 MeV proton and 116 MeV oxygen ions at different doses. It
was observed that the microstructural parameters such as domain size,
microstrain within the domain and dislocation density did not change
significantly with the increased dose for proton irradiated samples. A clear
change was noticed in these microstructural parameters as function of dose for
oxygen irradiated samples. The values of microstrain and dislocation density
increased significantly with the dose of irradiation.

XRD patterns of gamma irradiated and unirradiated
ciprofloxacin in solid state has been studied.\textsuperscript{146} XRD patterns of irradiated
powders showed less degree of crystallinity as evidenced by fewer peaks of
lower intensity, compared with non-irradiated sample. The characteristic of
diffraction peaks relevant to crystalline ciprofloxacin nearly disappeared with
increasing dose of radiation from 15 to 100 K Gy.

Investigation of the resistance of potassium copper nickel hexacyano
ferrate(II) ion exchanger\textsuperscript{147} against gamma irradiation suggests that there was
no significant change in the colour and X-ray diffraction of the exchanger upon irradiation.

Radiation effect on XRD of apocynum fiber has been investigated.\textsuperscript{148} The studies revealed that gamma irradiation could change the aggregate state of apocynum fiber and decrease their crystallinity. The intensity of the three crystal peaks (23\textdegree, 15\textdegree, and 17\textdegree) increased under a higher dose (280kGy) showing that gamma irradiation of a higher dose may break the macro molecular chain into shorter chains. The shorter the macromolecular chain, the easier it is to order apocynum fiber and to heighten the crystal peaks.

The changes in the supramolecular structure of pine wood cellulose treated by various doses (from 20 kGy to 9000 kGy) of gamma radiation have been investigated. With the increase in the gamma radiation of wood, both the crystallinity and the average size of the crystallites of cellulose decreased.\textsuperscript{149}

The effect of fast-neutron irradiation on some binary \(\sigma\) phases has been studied by X-ray diffractometry.\textsuperscript{150} Radiation damage is evident in line broadening of the diffraction lines, relative intensity changes and anisotropic changes in lattice parameter. X-ray diffraction studies reveal the change in lattice parameters in neutron irradiated carbon materials,\textsuperscript{151} CVD-diamond, silicon-carbide, and silicon,\textsuperscript{152} gamma irradiated NaCl, LiF,\textsuperscript{153} ammonium
tetrachlorozincate\textsuperscript{154} and Li\textsubscript{2}O-doped NiO solids\textsuperscript{155} and deuton irradiated germanium.\textsuperscript{156}

1.3.3. Summary of effect of radiation on XRD

Lattice defects caused by irradiation have a profound influence on the X-ray diffraction patterns of crystalline solids. The observed general effects are significant changes in the crystalline identity, relative intensity, crystallinity, lattice distortion and structural transformation. Systems in which no significant changes are produced have also been reported.

1.4. Electronic Spectral Studies

1.4.1. General

Electronic spectra of molecules are concerned with transition between electronic states. Transition metal complexes absorb radiation in the visible and UV region. The electronic transitions occur between levels whose spacings correspond to energy of visible-UV region. In metal complexes these transitions are frequently referred to as d-d transition since they involve molecular orbital with d-character.

1.4.2. Brief review of electronic spectra of irradiated materials.

The electronic absorption spectra of dithizone and its metal complexes of Hg, Cd and Zn doped in poly(methylmethacrylate) has been investigated before and after gamma irradiation.\textsuperscript{157} It is found that the complex formation
resulted in significant changes in both the position and the intensity of the electronic bands of dithizone. Gamma radiation causes remarkable decrease in the intensities of most of the absorption bands of the metal complexes. The rate of decrease depends on the nature of the metal.

Studies on the effect of gamma irradiation on the electronic spectra of irradiated and unirradiated 5-hydroxy-L-tryptophan and 5-hydroxy tryptamine in aqueous solution have been conducted. There is steady decrease in absorption intensities at 207, 275 and 222 nm with decrease in pH in the dose rage of 100-1500 Gy. The absorbance ratios at all these wavelengths indicate that 5-hydroxy-L-tryptophan is much less sensitive to break down by gamma irradiation as compared to that of 5-hydroxy tryptamine.

Gamma radiolysis of ampicillincobalt complex in aqueous solutions was studied at doses from 20 to 100 Gy, using a Cs source. The variations in UV and IR spectra due to their radiolysis were studied. The results showed an increase in absorbance values with increasing dose and this dependence is linear in the dose range studied.

Effect of gamma irradiation on cobalt(II) and nickel(II) complexes of diethylenetriamine have been reported. The bands in the UV spectra of irradiated samples are broad. This is possible only if the field strength fluctuates over a significant range of energy. The CFSE of the complexes are affected by irradiation as evidenced from the UV spectra of irradiated samples.
Electronic absorption spectra of Na$_2$S$_2$O$_3$H$_2$O has been studied before and after gamma irradiation.\textsuperscript{137} Unirradiated sample displays strong absorption bands at 245nm due to (n$\rightarrow$$\sigma^*$) absorption of S-S bond and at 340-360 nm due to the (n$\rightarrow$$\pi^*$) of the S = O bond. In the irradiated sample, only one absorption band due to n$\rightarrow$$\sigma^*$ of S-S bond appears whereas the absorption of S=O bond completely disappears. The S-S band suffers a pronounced red shift upon irradiation.

Spectrophotometric studies of sodium meta phosphate glasses doped with 3d transition metals (0.1\%Ti$\rightarrow$Cu) were carried out before and after successive gamma irradiation.\textsuperscript{160} In the undoped glass, strong charge transfer ultraviolet absorption bands are observed and are related to trace iron impurities in the raw materials used for glass preparation. These charge transfer bands are observed to mask characteristic ultra violet bands due to some of the transition metals. Gamma irradiation produces characteristic induced bands in the base undoped and transition metal doped phosphate glasses. The response of the glasses to gamma irradiation is related to the creation of numerous induced defect colour centers.

The UV - visible absorption spectra of virgin and gamma irradiated (20-800KGy) CR-39 polymer have been deduced.\textsuperscript{161} The existence of the peaks, their shifting and broadening as a result of gamma irradiation has been studied. The indirect and direct band gap in virgin and gamma irradiated
CR-39 has been determined. The values of indirect band gap have been found to be lower than the corresponding values of direct band gap.

Effect of γ-irradiation on the molecular properties of myoglobin has been discussed. UV-visible spectrum of myoglobin showed a typical spectrum of the protein that contained a heme group, which has an absorbance maximum around 409 nm. However, irradiation disrupted the heme group resulting in a decrease of the absorbance at 409 nm.

The UV-visible absorption spectra of nominally pure and transition metals-doped (Ti-Cu 0.1%) cabal glasses were measured from 200 to 1000 nm before and after successive gamma irradiation. The intensity of the radiation-induced bands depends on the number of intrinsic defects and the rate of formation of the different induced colour centers. Also, the possible photochemical processes due to the effect of radiation on the transition metal ions are observed to affect the overall induced spectra. γ-radiation effect on the absorption spectra of manganese phthalocyanine polymer thick films has been investigated. The optical parameters were obtained from the analysis of the absorption spectra over a wavelength range of 385-900 nm. It was observed that the increase in gamma radiation dose caused an increase in the optical density and also shift in the spectrum towards higher wavelengths.

UV-visible absorption spectra of gamma-irradiated and unirradiated poly(ethersulphone) and poly(ether ether ketone) films, 70 MeV carbon ion
irradiated Kapton-H polymer and electron irradiated barium strontium borate have been investigated.\textsuperscript{165-167}

Effect of swift heavy ion irradiation on tris(8-hydroxyquinoline) aluminium(Alq\textsuperscript{3}) thin films has been studied.\textsuperscript{168} Alq\textsuperscript{3} have been irradiated with swift heavy ion of Li\textsuperscript{3+} 40 MeV with various ion fluences. In UV-visible spectra of irradiated film, the absorption peak intensities of irradiated thin films decrease for increasing ion fluence.

1.4.3. Summary of effect of radiation on electronic spectra

Defects caused by irradiation influence the electronic spectra of materials. The observed significant changes are decrease in the intensity of the bands, shift in $\lambda_{\text{max}}$ and broadening of spectral bands.

1.5. Antimicrobial Studies

1.5.1. General

Radiation offers several advantages as a sterilization method that makes it attractive in a growing number of situations over the conventional methods of sterilization. Articles sterilized by radiation include a large variety of disposable medical products, sutures and implants, pharmaceuticals and cosmobiological tissues, and many other articles.\textsuperscript{169,170} Gamma radiation was proposed in the British Pharmacopoeia\textsuperscript{171} as a suitable steril method for sterilizing certain surgical materials and equipments.
1.5.2. Process of activating and inducing antimicrobial properties by irradiation

Process of activating or enhancing antimicrobial materials by irradiation with gamma rays and UV-radiations is a topic of recent interest. Antimicrobial coatings and powders and method of forming same on medical devices are provided. The coatings are formed by depositing an antimicrobial biocompatible metal by vapour deposition techniques to produce atomic disorder in the coating such that a sustained release of metal ions sufficient to produce an antimicrobial effect is achieved. The invention also extends to a method of activating or further enhancing the antimicrobial effect of antimicrobial materials formed with atomic disorder. It is also possible to irradiate materials initially formed with a level of atomic disorder, which is insufficient to produce an antimicrobial effect, such that the irradiated material has an acceptable antimicrobial effect. The process of activation comprises irradiating the material with a low linear energy transfer form of radiation such as beta or X-rays, but most preferably gamma rays. The antimicrobial material is preferably oriented substantially perpendicular to the incoming radiation. The level of activation may be further enhanced by irradiating the material adjacent to a dielectric material such as oxides of Ta, Al and Ti, but most preferably silicon.

1.5.3. Brief review on antimicrobial activity of irradiated materials.

The effect of $\gamma$ - irradiation on the antimicrobial activity of chitosan has been reported, against Escherichia Coli. Irradiation of chitosan at
100kGy under dry conditions was effective in increasing the activity and inhibited the growth of E.coli completely. Low dose irradiation, specifically 100kGy, gives enough degradation to increase its antimicrobial activity as a result of change in molecular weight. The molecular weight of chitosan significantly decreased with the increase in irradiation dose. Antimicrobial activity assay of chitosan fractionated according to molecular weight showed that $1 \times 10^5 - 3 \times 10^5$ fraction was most effective as antimicrobial agent. Chitosan whose molecular weight was less than $1 \times 10^5$ had no activity.

Effects of gamma irradiation on solid sulfonamides have been determined. There antibiotics sulfafurazole, sulfamethoxazole and sulfacetamide sodium belonging to sulfonamides were irradiated and changes in antimicrobial activities were studied at normal and accelerated stability test conditions. Antimicrobial activities of irradiated and unirradiated preparations were performed by the microdilution broth method, against S.aureus, E.coli and E.faeaalis. Irradiation did not produce any change in antimicrobial properties.

Studies on antibacterial properties of irradiated pyridoxamine led to the following observations. A new antibacterial agent is produced by irradiation of pyridoxamine under aerobic and anaerobic conditions. The potency of the agent found is critically related to the wavelength and duration of irradiation and to H ion concentration, temperature and concentration.
studies on antimicrobial activity of gamma irradiated ciprofloxacin\textsuperscript{146} revealed no change in activity.

Sterility and antibacterial activity of some pencillins and their salts, gramicidin and neomycin subjected to sterilization by gamma irradiation has been investigated. The results have proved that the pencillins analysed, gramicidin and neomycin can be sterilized by irradiation with a dose of 25kGy, without any detrimental effect on their properties and antimicrobial activity\textsuperscript{176}.

Amoxicillin trihydrate powder was irradiated at different doses of gamma irradiation and the subsequent changes in terms of physicochemical properties and potency were evaluated.\textsuperscript{177} The results indicated that dried powder of amoxicillin trihydrate is stable after sterilization by irradiation.

Antimicrobial activity of UV irradiated nylon film for packing applications has been investigated.\textsuperscript{178} Conversion of amide groups on the surface of nylon to amines having antimicrobial activity can be effected by using 193 nm UV irradiation.

Simple mixing of charge stabilized metallic nanoparticles with a photosensitiser results in enhancement of antimicrobial activity.\textsuperscript{179} Photosensitisers, such as toluidine blue O, act as light activated antimicrobial agents. Although they have no antimicrobial activity at low concentration in
the dark, when irradiated with light of a certain wavelength (such as 633nm for toluidine blue O) they are able to kill a wide range of microbes.

Antibacterial activities of acrylic acid-grafted polypropylene and its metallic salts have been studied. Acrylic acid was grafted onto polypropylene fabric by a pre-irradiation method using $^{60}\text{Co}$ gamma ray. Antibacterial activities of metallic complexes of acrylic acid grafted polypropylene fabrics were evaluated. A silver complexed fabric had strong biocidal effect for all bacteria. Fe, Cu and Zn complexed fabrics had different antibacterial activities depending on each bacterium.

Formation of antibiological substances by radiation chemical reaction and occurrence of antibacterial activity after gamma irradiation from two constituent moieties of the chloramphenicol molecule has been investigated.

The radioprotective effects of hesperidin, a flavonone glucoside subjected to 2Gy radiation were investigated by using the micronucleus test for anticlastogenic and cell proliferation activity. Irradiation reduced the frequencies of micronucleated polychromatic erythrocytes. The study demonstrates that hesperidin has powerful protective effects on the radiation induced DNA damage and on the decline in all proliferation activity.

Studies on antibacterial activity of argon fluoride excimer laser radiation on clinically important strains of Gram- negative bacteria have been conducted. Antibacterial activity was evaluated on two Acinetobacter
baumannii, one Enterobacter cloaceae, three Escherichia coli, two Helicobacter pylori, one Klebsiella pneumoniae and two Pseudomonas aeruginosa strains. The results showed that the total laser beam fluence was the most important parameter to consider in evaluating bactericidal effect. A critical value of the total fluence was determined for each strain, such that, for laser beam fluence greater than this critical value, no colonies appeared to survive while for laser fluences less than this critical value, the survival ratio did not exceed $22 \times 10^{-7}$ colony forming units.

The sterilization of honey with $^{60}$Co gamma radiation has been studied. Unprocessed honey is a recognized wound-healing remedy. However to make clinical use of honey acceptable, it should be sterile. Antibacterial activity increased with increasing dose of $\gamma$-rays and after a dose of 25 kGy, the antibacterial activity was not altered.

The effect of gamma irradiation on the antimicrobial activities of polyphenols of green tea leaf was studied. The anitmicrobial activities against staphylococcus aureus and streptococcus mutans were higher in the irradiated sample, which showed inhibition of microorganisms tested at a lower concentration than those of the non-irradiated sample. Results indicated that irradiation of polyphenols may maintain the biological activities and even increase the anti-microbial activity.
The effect of UV radiation on the antimicrobial activities of monocytes for the intracellular pathogen Mycobacterium avium intracellulare (MAI) has been studied. \textsuperscript{186} UV radiation augmented monocyte antimicrobial activity for MAI in a dose dependent fashion. UV radiation doses of greater than or equal to 25 J/m\textsuperscript{2} resulted in a 50-100 fold reducing of MAI growth. UV radiation acted directly to augment intrinsic monocyte antimicrobial activities.

Aromatic geranyl derivative, filifolinyl senecionate, isolated from the resinous exudate of Heliotropium filifolium has been found to show antibacterial activity against Escherichia coli K-12. \textsuperscript{187} After irradiation of a solution of filifolinyl senecionate with UV at 366 nm, the antibacterial activity was enhanced by 100%.

Potential possibilities of silver and gold nanoparticles embedded in composite films by irradiation, as antimicrobial coating against Escherichia coli \textsuperscript{188} and antifungal efficiency of hybrid silver nanoparticles synthesized by gamma irradiation \textsuperscript{189} have been studied. The hybrid silver nanoparticle can be used for antifungal agents.

1.5.4. Summary of effect of radiation on antimicrobial activity

Radiation sterilization of medical devices, drugs and pharmaceuticals are convenient, effective and economic. Antimicrobial properties of materials both natural and synthetic can be enhanced by irradiation in the solid state as well as in solution. Irradiation induces antimicrobial activity in certain materials while in some cases no change in activity is observed.
1.6. Scope of the present investigation

Thermal decomposition and the kinetics thereon have been extensively studied in irradiated crystalline solids containing oxyanions while inorganic complexes have received little attention in this area. However irradiation effects on thermal decomposition of a few complexes have been reported. In the present investigation effect of γ-radiation on non-isothermal decomposition kinetics of the following complexes have been studied.

1. Bis(diethylenetriamine) cobalt(II) nitrate
2. Bis(diethylenetriamine) nickel(II) nitrate
3. Bis(diethylenetriamine) zinc(II) nitrate
4. Bis(diethylenetriamine) cadmium(II) nitrate
5. Dinitrato bis(pyridine) cobalt(II)
6. Dinitrato bis(pyridine) nickel(II)
7. Dinitrato bis(pyridine) zinc(II)
8. Dinitrato bis(pyridine) cadmium(II)
9. Bis(2-aminopyridine) dinitrato cobalt(II)
10. Bis(2-aminopyridine) dinitrato nickel(II)
11. Bis(2-aminopyridine) dinitrato zinc(II)

Non-isothermal data have been analyzed by the integral method following Coats-Redfern equation assuming the order parameter ‘n’ as unity. Kinetic parameters E, A and ΔS were evaluated.
Literature survey revealed that effect of radiation on X-ray diffraction pattern have been investigated in many technologically important materials, simple inorganic salts and a few inorganic complexes. However such studies are lacking in \(\gamma\)-irradiated transition metal complexes. Therefore a study has been made to ascertain the changes in crystalline features brought about by irradiation in the following complexes.

1. Bis(diethylenetriamine) nickel(II) nitrate
2. Bis(diethylenetriamine) zinc(II) nitrate
3. Bis(diethylenetriamine) cadmium(II) nitrate
4. Dinitrato bis(pyridine) nickel(II)
5. Dinitrato bis(pyridine) zinc(II)

X-ray patterns were indexed by methods developed by R. Hesse and H. Lipson.

Effect of irradiation on the electronic spectra of various compounds have been studied but such studies are rare on transition metal complexes. In the present investigation the effect of gamma radiation on electronic spectra of the following complexes are studied.

1. Bis(diethylenetriamine) cobalt(II) nitrate
2. Bis(diethylenetriamine) nickel(II) nitrate
3. Dinitrato bis(pyridine) cobalt(II)
4. Dinitrato bis(pyridine) nickel(II)
5. Bis(2-aminopyridine) dinitrato cobalt(II)
6. Bis(2-aminopyridine) dinitrato nickel(II)

From the electronic spectral data Racah parameter \(B^1\) and covalency factor \(\beta\) of the complexes were calculated by graphic method.
A search of the available literature shows that irradiation is capable of changing antimicrobial properties of materials, both synthetic and natural. However such studies are lacking in γ-irradiated transition metal complexes. Hence it was of interest to investigate the antimicrobial properties of gamma irradiated transition metal complexes. In the present work antimicrobial properties of the following complexes were studied before and after gamma radiation by disc diffusion method.

1. Bis(diethylenetriamine) zinc(II) nitrate
2. Bis(diethylenetriamine) cadmium(II) nitrate
3. Dinitrato bis(pyridine) zinc(II)
4. Dinitrato bis(pyridine) cadmium(II)
5. Bis(2-aminopyridine) dinitrato zinc(II)