Introduction

The constantly growing demand of the well-dressed devices for an advanced civilized society has revitalized our curiosity for magnetism and has generated a stipulate to combine the different aspects of magnetic and electrical properties of materials. Over the last few years there has been insurgence in the research field of oxide materials, demonstrating miscellaneous behaviors such as dielectric, ferroelectric, magnetic and multiferroic properties. Many of our modern technological devices spread on such materials; these include memory devices, functional sensors, electrical power generator, transformers, electric motors, television, telephone, computers and components for sound and video reproduction systems etc. The momentum in the research is attributed to the multifunctional properties of these materials, which have prosperity to enrich the present technology. These properties appear from the coupled action of charge as well as spin character of electrons, providing a coalition of electrical and magnetic properties in the same material. The recent developments in the characterization techniques and the materials processing techniques have provided the thrust to broaden domain of materials functionality. One of the novel field emerging, because of the ever growing demand from the contemporary industries for smart materials possessing all round performances, are the multiferroic materials occurring as a result of coupling among elasticity, charge and spin degree of freedoms. There are certain specific advantages of multiferroics over other oxides emanating from the coupling between the magnetic and dielectric properties because of the spin lattice coupling, which can only be harnessed if the corresponding devices can be realized in practice.

Aim of present work and thesis outlines

There are two main aims of the present thesis: (i) to develop new multiferroic materials and (ii) upgrade electrical and magnetic properties of the host matrix (Mg-Mn ferrite) by the substitution of the tetravalent ($3d^0$) transition cation and swift heavy ion irradiation.

It is well known that the substitution of the tetravalent cations in the ferrite matrix upgrades their structural, electrical and magnetic properties, particularly $3d^0$ configuration plays an important role in the foundation of non centro-symmetry which is basic condition for introducing ferroelectricity in the material. So, it is interesting to study that the doping effect of Ti^{4+}, which may introduce ferroelectricity in the Mg-Mn ferrites which are already ferrimagnetic at room temperature. Effect of the doping of Ti^{4+} has been studied in the context of the structural, electrical, electronic structure and magnetic properties of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ ferrites.

The interest in the swift heavy ion (SHI) irradiation on these materials is because of the fact that SHI irradiation is well known technique for the structuring the surface of the films and modification in their structural, electrical and magnetic properties. It is known that magnetic property of the ferrite materials depends on the superexchange interactions, which are highly sensitive to any disorder in the ferrite materials. SHI has been proved a good source to produce a wide variety of defects, known to create structural strain and disorder in oxide materials responsible to modify their physical properties.

Bulk samples of basic composition $Mg_{0.95}Mn_{0.05}Fe_{2-2x}Ti_{2x}O_{4\pm\delta}$ $(0 \leq x \leq 0.5)$ were synthesized using conventional solid-state reaction technique; whereas the polycrystalline thin films of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ at different substrates have been grown using Pulsed Laser Deposition (PLD) technique. The structural, electrical, electronic structure and magnetic characterization of the prepared bulk materials have been performed using different techniques such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS), Dielectric Spectroscopy, Mossbauer Spectroscopy and dc Magnetization measurements. Thin films were characterized using X-ray diffraction, Atomic Force Microscopy (AFM), Magnetic Force Microscopy (MFM) and dc magnetization.

The complete thesis has been divided into six chapters.

Chapter 1 deals with a brief description of the origin of magnetism and definition of its subcategories such as; the phenomenon of diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. Apart from all these, ferrites, dielectric and ferroelectric materials are also discussed in order to understand a phenomenon where both magnetism (ferromagnetism/and antiferromagnetism) and ferroelectricity co-exist known as multiferroic materials.

Chapter 2 covers the necessary theoretical background and experimental details about the various techniques related to structural electrical and magnetic properties of the systems studied along with an overview about the swift heavy ion (SHI) irradiation such as its production and application. This chapter also covers the instrumental setup development work carried out during this course of thesis; such as the automated dielectric measurement and electric field versus polarization (E-P) measurement setup.

Chapter 3 comprises all the experimental results of bulk samples prepared by the solid-state reaction technique. The XRD analysis of $Mg_{0.5}Mn_{0.05}Fe_{2-2x}Ti_{2x}O_4$ indicates that all samples exhibit a single phase nature with structural transition from cubic spinel to tetragonal due to Ti substitution. This structural transformation also confirmed from the increase in unit cell volume. Because with the substitution of Ti ions, the Fe^{3+} to Fe^{2+} conversion is taking place to maintain the charge neutrality in the system. The dispersion behaviour observed in dielectric constant as a function of frequency has been explained according to interfacial polarization as predicted by the Maxwell-Wagner and Koop's phenomenological theory. The composition dependent dielectric constant found to increase with the increase in the concentration of Ti ions up to 20% (x = 0.2) and has been explained in terms of hopping (exchange) of electron between Fe^{2+} and Fe^{3+} ions which indicates that the polarization in these materials is similar to conduction process in ferrites. It is observed that ac and dc conductivities are also increasing with substitution up to x = 0.2 and after that it decreases systematically. The exponent (*s*) of power law behaviour of ac conductivity ($\sigma_{ac} = A\omega^s$), which refers to the measure of charge correlation, was calculated and found to be in the range of 0.5-0.8. The observed peaks in the capacitance versus temperature study suggest the ferroelectric transition in these materials. Therefore, from this observation of the capacitance behaviour, we can propose that these materials exhibit multiferroic property.

From the Mossbauer studies it has been concluded that the quadrupole interaction increases, whereas the magnetic hyperfine interaction decreases with the increase in the concentration of the non-magnetic ion (Ti^{4+}). The dc magnetization hysteresis loop study reveals that up to 50% substitution, all systems exhibits ferrimagnetic behavior at or above room temperature and saturation magnetization decreases with increasing the concentration of Ti^{4+} ions due to the dilution of the B-sublattice by Ti ions. The zero field cooled (ZFC) and field cooled (FC) magnetization study also infer that up to 50% doping of Ti ions, systems exhibit a ferrimagnetic ordering at room temperature and with further increase in Ti ions (at 60%) substitution, ferrimagnetic transition temperature decreases to 280 K. This decrease in the transition temperature may be attributing to the fact that the replacement of antiferromagnetically coupled neighbor with non-magnetic Ti^{+4} ions will lead the dilution of the sub-lattice (the spin reduction) as a result the exchange interactions between the magnetic ions get weakened and as a consequence the transition temperature decreases.

The NEXAFS study clearly indicates that the doping of Ti^{4+} ions modifies the electronic structure of these systems. The O K-edge spectra of pure (x = 0.0) sample indicates that low energy features resembles with Fe_2O_3 but after the doping of Ti, it is clearly seen that the doublet feature of Fe_2O_3 has changed to feature like FeO. This infers that Fe^{3+} changes to Fe^{2+}, which is in consistent with transport studies. The Fe K-and $L_{3,2}$ edge spectra also confirmed that with the substitution of Ti^{4+} ions, Fe^{3+} is converted into Fe^{2+}. The Ti $L_{3,2}$-edge NEXAFS spectra of the entire compositions split into L_3 and L_2 regions due to spin orbit interactions, reflecting transitions of Ti 2*p* core electrons into Ti 3*d* states in the conduction bands. The separations between various observed peaks well match with Ti^{4+} 2p-edge spectra in O_h symmetry calculated by de Groot *et al.* The estimated value of 10 *Dq* for this entire series is approximately 2.1 eV, which implies that the valency of Ti in all composition remains in +4 state. Finally, we can say that the Ti substitution induces multiferroic properties in these materials, which are in well agreement with our earlier reported results.

Chapter 4 gives information about the structural and magnetic properties of thin films and its comparison with the bulk sample of the same composition. From analysis of the XRD pattern of bulk Mg-Mn ferrite, it is observed that all the diffraction peaks represent a polycrystalline single phase cubic spinel. All peaks as observed in the bulk sample, are not found in the thin films and the intensities of the peaks are also quite different from the bulk; for example, (311) is the lowest intensity peak in the thin films, whereas, it is of highest intensity peak in the bulk sample. Moreover, from the XRD study, it is observed that the film deposited on ITO has smaller grain size than the film deposited on Pt-Si. DC magnetization hysteresis loop measurement study shows that the bulk sample of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ and its thin film deposited on platinum coated silicon (Pt-Si) substrate shows a well defined hysteresis loop at room which reflects its ferrimagnetic behavior at room temperature. However, the film deposited on the indium tin oxide coated glass (ITO) substrate does not show any hysteresis (passes through the centre) loop at room temperature, which infers its superparamagnetic behavior at room temperature. From the analysis of AFM micrograph it is found that film deposited on ITO (R.M.S. roughness ~0.40 nm) is smoother than that of the film deposited on Pt-Si (R.M.S. roughness ~1.27 nm). The 2D PSD spectra of both the films are almost flat which indicates that the surface of the films is featureless. A systematic decrease in the corresponding root mean square

(R. M. S.) phase shift as a function of tip lift height indicates that these thin films having a good magnetic structure which is further supported by the magnetization data.

Chapter 5 is all about the irradiation studies on the thin films using 200 MeVAg^{15+} ions. This chapter also includes the comparative studies on the unirradiated and irradiated films deposited at different substrate. The thin films of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ deposited at various substrates were irradiated using 200 MeV Ag^{15+} ion beam. From the x-ray diffraction analysis, It has been found that the film deposited on Pt-Si exhibit single phase cubic spinel structure before and after the irradiation with lattice constant a = 8.23Å. In addition, after irradiation intensity of peaks increases and is maximum at a fluence value 1×10^{11} ions/cm^2 and after this fluence intensity of peaks decreases due to SHI irradiation induced defects. However, Mg-Mn ferrite thin films grown on ITO, shows that after SHI irradiation grain size decreases, which may be due to stress-induced grain fragmentation.

From the analysis of the AFM micrograph of the film deposited on Pt-Si, it is found that as the film is irradiated at fluence (Φ) 1×10^{11} ions/cm^2, surface morphology is dominated by structure (these structures are like pillars). From the size distribution of the magnetic pillars calculated from the AFM micrograph, it is found that at fluence 1×10^{11} ions/cm^2, these pillars have two types of size distribution ~63 nm and 129 nm. As the fluence increases to 5×10^{11} ions/cm^2, the size of the pillars increases in both lateral and vertical directions and at 1×10^{12} ions/cm^2, size of the pillars decreases laterally whereas height (vertically) increases and the density of the pillars also decreases. The value of the rms surface roughness is also been found to increase from 1.27 to 8.95 nm with the fluence values. 2D PSD spectra calculated from AFM micrograph indicate that film irradiated with 200 MeV Ag^{15+} exhibits peaks, indicating that the surface of the films is dominant by the structures. From the PSD spectra it can be seen that intensity of plateau height (w) increases as the fluence value increases, which is compliment to the of the increase of the height of pillars and roughness of the film. The observed value of the roughness exponent (α) and growth exponents (β) indicate that the capillary forces and the surface diffusion are dominant mechanisms to produce the structure after the irradiation.

From the analysis of the AFM micrograph of the film deposited on ITO, it is observed that the rms surface roughness decreases with increase in ion fluence. The decrease in the rms roughness value clearly indicates that a film deposited on ITO has become smoother after the irradiation.

From dc magnetization hysteresis loop study, it is observed that the film deposited on Pt-Si exhibits a ferrimagnetic ordering at room temperature and the saturation magnetization increases with fluence value up to 5×10^{11} ions/cm^2 due to grain growth and increase in crystallinity of the film (i.e., the system gets more ordered). However, with further increase in fluence value, the magnetization decreases, but this value is still larger than that of as-deposited film. This decrease in the saturation magnetization after an optimum fluence 5×10^{11} ions/cm^2 may be due to the following reasons: (i) decrease in the size of magnetic pillars and (ii) redistribution of cations among the sub-lattices.

The film deposited on ITO exhibits a superparamagnetic behavior before and after the irradiation at room temperature due to its nano-crystalline behavior. However, it has been observed that after irradiation, the magnetization decreases with irradiation fluence, which may be due to the redistribution of cations and decrease in the grain size caused by SHI irradiation. From the magnetization (M) versus temperature (T) curves, it is observed that after irradiation blocking temperature decreases systematically with increase in fluence value, and reaches to a value 200 K at the highest fluence (1×10^{12} ions/cm^2). This may be due to the reduction in grain size after irradiation as observed in the x-ray studies.

From the MFM images of the film deposited on Pt-Si, it is observed that film irradiated at fluence 5×10^{11} ions/cm^2 shows a maximum magnetic contrast, which is in good agreement with magnetization data. Moreover, the domain seems to be oriented along some particular direction. On the contrary, with further increase in fluence, the magnetic contrast decreases. From the analysis of MFM data of the film, deposited on ITO, it is observed that phase-shift increases from 0.14° (for as-deposited thin film) to 0.42° (for irradiated film with fluence value of 1×10^{11} ions/cm^2), which indicates that the magnetic signal increases with irradiation and with further increase in the fluence value to 5×10^{11} ions/cm^2, its value found to decrease systematically and attains a value of 0.11° at highest fluence.

Finally, chapter 6 presents an overview of the results concluded from all previous chapters and scope of future work on the studied materials.