Chapter 6

Summary and Future Scope

This chapter present the summary of the work carried in this thesis and future scope of the present work.

6.1 Scope of the Present Work

Substitution of the tetravalent transition metal cation with $3d^0$ configuration (Ti^{4+}) in spinel ferrites provides interesting structural, electrical, electronic structure and magnetic properties. Work presented in this thesis relates studies on structural, electrical, electronic structure and magnetic properties of Ti doped $Mg_{0.95}Mn_{0.05}Fe_2O_4$ ($0 \leq x \leq 0.5$) spinel ferrite. We have synthesized the bulk and their thin films of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ using Pulsed Laser Deposition (PLD) method onto Pt-Si and ITO substrates. In addition to this, swift heavy ion irradiation (SHI) has been also used for material modifications. Since it is well known that SHI irradiation generate different types of controlled defect states namely point defects ($S_e < S_{eth}$, S_{eth} is the electronic threshold value of the material), extended point defects ($S_e \sim S_{eth}$) and amorphized latent tracks ($S_e > S_{eth}$), which modify the structural and magnetic properties. Beside these properties, SHI irradiation is also used for engineering the patterns of thin film surface.

Considering all above mentioned methodology the present thesis aims:

1. *Substitution of tetravalent transition metal cation ($3d^0$ configuration i.e. Ti^{4+}) in* $Mg_{0.95}Mn_{0.05}Fe_2O_4$ spinel ferrite, in order to introduce ferroelectricity and also to understand modification in structural, electrical, electronic structure and magnetic (i.e. various magnetic exchange interactions) properties.

2. From the application point of view, the synthesization of the polycrystalline thin films and their growth optimization using Pulsed Laser Deposition (PLD) techniques and their characterization.

3. Further to investigate the effect of controlled defects created by swift heavy ion (SHI) irradiation on the structural and magnetic properties as well as engineering the micro/nano patterns by the swift heavy ion irradiation.

6.2 Effect of Ti^{4+} Substitution in $Mg_{0.95}Mn_{0.05}Fe_2O_4$

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 method. The doping effect of Ti^{4+} ions on structural, electrical, electronic structure and magnetic properties has been studied 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.

A resume of main findings drawn from the present work can be summarized in following points

(i) The XRD results indicate that the substitution of Ti ions creates non centro-symmetry as result system transform from cubic to tetragonal phase. This is also confirmed from the increase in unit cell volume with the Ti ions substitution. The Fe^{3+} to Fe^{2+} conversion is taking place to maintain the charge neutrality in the system due to the Ti^{4+} substitution.

(ii) The capacitance study as a function of temperature clearly indicates the signature of the ferroelectricity in the present systems. The dispersion behavior observed in dielectric constant as a function of frequency has been explained according to interfacial polarization as proposed by the Maxwell-Wagner and Koop's in their phenomenological theories.

(iii) Mossbauer spectroscopy study indicates that quadrupole interaction increases whereas the hyperfine field decreases with an increase in the concentration of non-magnetic ion (Ti^{4+}). The emergence of the electric field gradient infers the distortion in the cubic symmetry caused by the Ti ions.

(iv) The dc magnetization hysteresis loop study reveals that up to 50% substitution, all systems exhibit ferrimagnetic behaviour 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 attributed 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 consequence the transition temperature decreases.

(v) 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 resemble 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 means that Fe^{3+} changes to Fe^{2+} which is 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+} converted to 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 separation between various observed peaks well matches 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 +4 state.

We conclude that the Ti^{4+} substitution proposes these materials bearing multiferroic properties [see Ref. 52, 53 in Chapter 3].

6.3 Thin Films of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ Deposited on Pt-Si and ITO Substrates

Thin films were characterized using X-ray diffraction, Atomic Force Microscopy (AFM), Magnetic Force Microscopy (MFM) and dc magnetization. The results of the comparative study of bulk and thin films deposited at different substrates of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ ferrite thin films by pulsed laser deposition (PLD) leads to following conclusions:

(i) 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. However, the appearance of peak (222) as a dominant peak in the film deposited on Pt-Si signifies a slow texturing in the thin film form. Moreover, the film deposited on ITO has smaller grain size than the film on Pt-Si.

(ii) 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.

(iii) From the analysis of AFM micrograph, we have found that film deposited at ITO (R.M.S. roughness ~0.40 nm) is smoother than that of the film deposited at Pt-Si (R.M.S. roughness ~1.27 nm). 2D PSD spectrum is almost flat for the films which clearly indicate that both films are featureless. A systematic decrease in the corresponding root mean square (R. M. S.) phase shift in the vibration frequency of the cantilever as a function of tip lift height indicates that these thin films have good magnetic structure which is further supported by the magnetization data.

6.4 Effect of 200 MeV Ag^{15+} Ions Irradiation on the Thin Films of $Mg_{0.95}Mn_{0.05}Fe_2O_4$ Deposited at Different Substrates

Results on irradiation by 200 MeV Ag^{15+} ions beam can be summarized as:

(i) From the XRD study, we have observed that the both set of the films exhibits a cubic spinel structure before and after the SH irradiation. In addition to this it is observed that the intensity of peaks, of the film deposited on Pt-Si, increases and is maximum at a fluence value 1×10^{11} ions/cm^2 and after that decreases with further increase in fluence due to SHI irradiation induced defects. However, Mg-Mn ferrite grown on ITO shows that after the SHI irradiation grain size decreases which may be due to stress-induced grain fragmentation.

(ii) The AFM micrograph of the films deposited on Pt-Si indicates that as the film is irradiated at fluence (Φ) 1×10^{11} ions/cm^2, surface morphology is dominated by magnetic pillars and with further increase in fluence value, size of the structures increases. At fluence value of 5×10^{11} ions/cm^2, size of the structures increases in both lateral and vertical directions, whereas at 1×10^{12} ions/cm^2, size of the pillars decreases laterally, height (vertically) increases and density of pillars decreases. The value of the rms surface roughness has also been found to increase from 1.27 to 8.95 nm with the fluence values. 2D PSD spectra indicate that film irradiated with 200 MeV Ag^{15+} ions exhibit peaks which indicating that the surface of the film is dominant by the structures. From the PSD spectra, it is observed that intensity of plateau height (w) increases as the fluence value increases which infer that the height of pillars and roughness of the film increases. The observed value of the roughness exponent (α) and growth exponents (β) indicate that the capillary forces and the surface diffusion are dominating processes during the ion 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 the ion fluence value. The decrease in the rms roughness value clearly indicates that films deposited on ITO become smooth after the irradiation.

(iii) DC magnetization hysteresis loop measurement shows that the film deposited on Pt-Si exhibits a hysteresis loop before and after the irradiation at room temperature. It is observed that the saturation magnetization increases with fluence value up to 5×10^{11} ions/cm^2 due to grain growth and increase in crystallinity i.e. the system gets more ordered. However, with further increase in fluence value, the magnetization start decreasing, but this value is larger than that of as-deposited film. The decrease in the saturation magnetization after an optimum fluence 5×10^{11} ions/cm^2 may be due to the following effects: (i) decrease in the grain size and (ii) redistribution of cations among the sub-lattices.

The film deposited on ITO exhibits superparamagnetic behavior before and after the irradiation at room temperature due to its nano-crystallinity. However, it is observed that the magnetization decreases with irradiation fluence, this may be due to the redistribution of cations and reduction 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 an increase in fluence value, and reaches a value of 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.

(iv) From the MFM micrographs of the film deposited on Pt-Si, it is observed that film irradiated at fluence value 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 irradiation fluence, the magnetic contrast decreases.

From the MFM images 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.

6.5 Future Scope

We want to mention that the measurements such as high temperature dc magnetization and Mossbauer spectroscopy will provide us information about magnetic ordering in these materials near and above the Neel temperature. Electric field versus polarization (E-P) will provide more insight about the ferroelectricity in these materials. The epitaxial growth of thin films of these materials in different condition and different substrates and their characterization by Conversion Electron Mössbauer Spectroscopy (CEMS) and dc magnetization data at low temperature in ZFC and FC modes would be of great help for the deep understanding of thin film systems. The deposition of the epitaxial thin films of Ti doped system and its characterization by dielectric and E-P measurement will be a good study in the context of multiferroicity of these systems. In addition, 200 MeV Ag^{15+} irradiated thin films show an increase in the saturation magnetization after irradiation up to certain fluence. More interesting is the structuring of the surface after the irradiation. Therefore, there is a good scope to exactly optimize the energy and the fluence value of the ion and to see their effect in the saturation magnetization and in pattern formation in the thin films grown on different substrates and in different deposition conditions.

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