Summary

During the last few years there has been an extensive study in the direction of search for the materials possessing ferromagnetic as well as the semiconducting properties in view of their potential applications in the spin based electronics i.e. spintronics devices, wherein the spin controlled electrical, optical and magnetic properties are exploited. Ferromagnetic semiconductors possess a great potential for use as a source of spin polarized carriers and offer easy integration with semiconductor devices.

As an effort in the aforesaid venture we have studied structural, electrical and magnetic properties of two systems, namely, Ni doped LaFeO₃ (bulk and thin film) and Fe₃O₄ (thin films). On the basis of our observations we have proposed that the present studied systems are useful for spintronics. Our findings are summarized in this chapter.

6.1 Ni DOPED LaFeO₃

LaFeO₃ (a 3d transition metal oxide) is an antiferromagnetically ordered insulator at room temperature (Néel temperature, Tₙ=740 K) with Fe³⁺ ions in an orthorhombic environment and with a charge transfer gap of 2 eV. A wide range of electrical and structural properties have been observed by changing the concentration of charge carriers in perovskites LaFe₁₋ₓNiₓO₃, where x is the fraction, representing doping.

6.1.1 Bulk

We have synthesized single phase samples of LaFe₁₋ₓNiₓO₃ (0 ≤ x ≤ 0.6) materials using solid-state reaction route and studied their structural and electrical properties. The x-ray diffraction exhibits single-phase orthorhombic structure for all studied samples. The structural analysis was
carried out using PowderX and Rietveld refinement programme (FullProf software) with space group *Pnma* up to the 60% substitution level. It was found that on substituting Ni at the Fe site the lattice parameters changed considerably but doped systems remain in the orthorhombic symmetry with space group *Pnma*. The unit cell volume decreases with the Ni concentration and reached a value of 190.705 Å³ for 60% doping (LaFe₀.₄Ni₀.₆O₃), while in the case of pure LaFeO₃ the value is 238.982 Å³. The electronic structure was investigated using x-ray absorption near edge structure (XANES) spectra at O K-*, Fe L₂,₃*- and La M₄,₅*-edges. On substitution of Ni at Fe site in LaFeO₃, the O K-edge spectra show a new structure about 2.0 eV lower than O K-edge of LaFeO₃. This new feature grows as the concentration of Ni is increases. The observation is consistent with the behaviour of resistivity data, which show that the resistivity decreases very fast with Ni substitution from GΩ-cm for LaFeO₃ to a few mΩ-cm for the sample with 60% Ni substitution. The resistivity data have been analyzed using Mott’s variable range hopping (VRH) model and it is found that the gap parameter decreases systematically with the Ni substitution. From the Fe L₂,₃*-edge structures we have found that the Fe ions are in the trivalent state. The observed features have been explained on the basis of charge carrier doping in LaFeO₃. On the basis of the above-mentioned observations, we infer that the disorder-induced localization effectively controls the resistivity behaviour.

### 6.1.2 Thin Films

We have studied the structural, electrical and magnetic properties of highly c-axis oriented single-phase epitaxial thin films of LaFe₁₋ₓNiₓO₃ (x = 0.3, 0.4 and 0.5) grown on [001] oriented LaAlO₃ (LAO) substrate using pulsed laser deposition (PLD) technique. We notice that the peak separation decreases with the increase in Ni concentration indicating a decrease is lattice mismatch. Small values of FWHM observed for these films indicate to the high crystalline quality of the film. From the structural characterization, we infer that the films grown on [001] LAO substrate are under the in-plane compressive strain and highly c-axis oriented single-phase epitaxial films. All these samples exhibit semiconducting behaviour, while their resistivity...
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values decrease with increase in the Ni concentration in the composition due to decrease in the energy gap. The resistivity data fits well for all the samples in the VRH model signifying that the conduction is controlled by the disorder-induced localization of charge carriers. We observe a clear magnetic hysteresis loop with coercivity ~110 Oe for all the samples at room temperature, establishing thereby their ferromagnetic nature. Their magnetization decreases with increase in the Ni concentration in the composition because of the increased number of itinerant d electrons ready to participate in the hopping interaction and thus decreasing the number of localized d orbital moments. The correlation between the electrical and magnetic properties in the present system projects it as a potential candidate for the spintronics oriented devices wherein the communication between the charge and the spin is desirable. Finally, we have studied the 1/f conduction noise properties in these thin films. The spectral density of noise voltage $S_v$ shows an inverse dependence on the frequency ($1/f^x$, $x \sim 0.8-1.1$) and the quadratic dependence of the bias current at room temperature for 10 Hz. All the samples show this behaviour throughout the studied temperature range (77-300 K), suggesting the noise to be of the conduction fluctuation type.

6.1.3 Swift heavy ion (SHI) irradiation effect on Ni doped LaFeO₃ thin films

The thin films were irradiated at room temperature with 190 MeV Ag¹⁵ ions using the 15UD tandem accelerator at Inter-University Accelerator Centre (IUAC), New Delhi with a range of fluence values (5x10¹⁰ - 1x10¹³ ions/cm²). We have shown that 190 MeV Ag¹⁵ irradiation can modify the structural vis a vis the electrical and magnetic transport behaviour of LaFe₀.₅Ni₀.₅O₃ thin films. After irradiation a systematic variation in the lattice parameter with the fluence is noticed and it can be found that for the highest irradiation dose, c parameter moves close to the bulk value, indicating that with irradiation the lattice of the composition relaxes. The irradiation induced lattice relaxation characterizes the composition with a lower resistivity and a higher magnetization value. We feel that the enhancement in the magnetization in the irradiated samples of LaFe₀.₅Ni₀.₅O₃ (the half mixture state of LaFeO₃ and LaNiO₃) may be due to the enhancement in the strain
induced canted antiferromagnetic interaction between the transition metal ions. A similar trend is manifested in the out of plane hysteresis loop measurement. From these studies it is evident that the irradiation with swift heavy ions can not only make the composition more semiconducting but can also enhance the magnetization. Also after the irradiation, the lattice of the composition relaxes, but the strain relative to that in the substrate enhances. These observations suggest that irradiation induced relaxation/strain relative to that in the substrate lays the foundation for the enhancement in magnetization and reduction in resistivity.

6.2 Fe₃O₄ THIN FILMS

Magnetite, Fe₃O₄ is the oldest magnetic material known to man. The electron transport in Fe₃O₄ is predicted to be fully spin-polarized such that it is half metallic. This combined with the fact that the Curie temperature is very high, makes Fe₃O₄ a very interesting candidate for spin valve applications. The spin-valves have received a lot of attention due to their application in magnetic recording read heads. As discovered few years ago, that epitaxial Fe₃O₄ films consist of structural domains, separated by anti-phase boundaries (APBs). It was postulated that the magnetic coupling across the APBs is antiferromagnetic, which strongly influences the spin-polarized conduction electrons.

In summary, we have grown the epitaxial Fe₃O₄ thin films of various thicknesses 15, 40 and 70 nm on MgO (100) substrate by molecular beam epitaxy (MBE) techniques. The conditions for growing the films were settled so that antiphase boundaries may be produced. Further, we have demonstrated that the presence of APBs in Fe₃O₄/MgO hetero-epitaxy strongly influences the charge transport properties. The samples were thoroughly characterized using high-resolution x-ray diffraction (HRXRD) and Raman spectroscopy techniques. The unit cell volume of the films calculated from a₁₁ and a₁ obtained from the HRXRD measurements was found to be the same as that of the bulk magnetite, suggesting that the films are stoichiometric. To estimate the density of APBs we performed magnetization measurements on these samples. It is clearly evident that the magnetization does not saturate with the maximum field of 1 tesla available.
with the instrument. The resistivity studies showed that 70 and 40 nm films possess the Verwey transition at 104 K and 95 K respectively, whereas it is absent in the 15 nm films. The resistivity of the magnetite thin films was found to be higher than the bulk resistivity (~1 mΩ-cm). The enhancement in resistivity of the magnetite thin films is related to the presence of epitaxial stress and APBs. The low frequency noise was found to scale inversely with the frequency i.e., \( \frac{1}{f^a} \) with \( a \) close to unity. The influence of APB related structural disorder on the low frequency charge dynamics is reflected in the temperature and thickness dependence of noise. The normalized noise, \( S_n/V^2 \), showed a hump at low temperature for all the films. We interpret this as an indication of the long-range electronic correlations associated with the Verwey transition, though these correlations were not evident in the resistivity behaviour. In order to get a fair idea about the size of APB we have performed magnetic force microscopy (MFM) on these films. The average domain size estimated for the films are found to be 50 and 100 nm for 40 and 70 nm thickness films respectively. The increase in domain size is consistent with the magnetization measurements which shows that the volume fraction of the films consisting of frustrated spin configuration decreases with the increase in film thickness.

6.2.1 SHI irradiation effect on Fe₃O₄ thin films

The thin films of thickness 70 nm were irradiated at room temperature with 190 MeV Ag\(^{15}\) ions using the 15UD tandem accelerator at Inter-University Accelerator Centre (IUAC), New Delhi with a range of fluence values (5\(\times\)10\(^{10}\) - 1\(\times\)10\(^{13}\) ions/cm\(^2\)). From our present studies, we infer that at low fluence the swift heavy ion irradiation modifies the strain state of the films and cation distribution in the vicinity of APBs whereas, at higher fluence it introduces structural disorder and transforms the phase from magnetite to maghemite. We found that the Verwey transition temperature \( T_v \) of these films increases with the ion fluence values from 109 K (for pristine) to 117 K for the film irradiated with 5\(\times\)10\(^{11}\) ions/cm\(^2\). Our explanation to this result is that the SHI irradiation changes the structure of the antiphase boundaries, possibly even anneals out some of the boundaries. However, at higher fluences the films do not show Verwey transition down to 77 K and the
resistivity value is higher than that of the pristine film, demonstrating again that the SHI irradiation induced structural disorder in the film (in agreement with XRD results). The results indicate strong dependence of the Verwey transition on the onsite Coulomb potential, interionic Coulomb potential and the bandwidth. All these parameters depend on the valence state of Fe at APB, the nature of strain in the system and the local stoichiometry. The magnetization results are also in agreement with the HRXRD and resistivity results. The isothermal magnetization hysteresis are intrinsically bulk measurements and the model proposed in this work addresses the irradiation induced structural transformation and modification of strain state, which consequently affects the cationic arrangements at APBs.

It is further established that by selecting appropriate irradiation parameters, i.e. by keeping the electronic energy loss below the threshold value for the columnar defect formation, one can tune the material properties to get an optimum Verwey transition temperature and maximise magnetization in the system. Finally, we have demonstrated that the phase transformation can be set in just by varying the ion fluence.

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