CHAPTER 5

ELECTRON SPIN RESONANCE AND MAGNETIC PROPERTIES OF HEAVY ION IRRADIATED LPMO SINGLE CRYSTALS

5.1 INTRODUCTION

It is well known that energetic ions create changes in a material along their track. These changes in structural and chemical can be used to alter the material’s properties (Cuomo et al 1989, Spohr 1990). When very high-energy ions are used, an in-depth modification can be achieved. So far, one of the most important parameters of ion beam techniques, apart from ion mass, is the kinetic energy. A few techniques even use GeV, creating long ion tracks for special applications (Spohr 1990). It determines the effect of ion irradiation and, directly, the thickness of the modified zone. The treatment of the mechanism of colossal magnetoresistance (CMR) is based on the concept of spin polarized transport, which implies that spin scattering on different magnetic inhomogeneities gives an essential contribution to the resistance. Application of large fields that smooth out these magnetic inhomogeneities results in reduction of the spin scattering and thus in the negative magnetoresistance.

The fact that in manganites the same carriers perform both charge transfer and magnetic exchange between the ions, i.e., work as transport and
magnetic order agents simultaneously, makes the magneto-resistance especially large in these materials. Most of the experiments confirm such a physical picture emphasizing the role of magnetic inhomogeneities. Resonance methods can give useful information on the internal dynamics of those materials, especially near the Curie temperature $T_c$, where they show the highest value of CMR effect (Li and Yuan 2004). Electron paramagnetic resonance (EPR or ESR) has been studied in a variety of lanthanum manganites (Rivadulla et al 1999, Volkov et al 2006). The temperature dependence of ESR line width is attributed to a spin-phonon interaction (one-phonon relaxation process) (Rettori et al 1997, Lofland et al 1997) or explained by spin-lattice relaxation of exchange coupled $\text{Mn}^{3+}$–$\text{Mn}^{4+}$ spin systems under the condition of a strong relaxation bottleneck model (Shengelaya et al 2000). The temperature dependence of ESR line width is also explained by the spin–spin (exchange) interaction (Tovar et al 1998). Suppression of ferromagnetic property and the Curie temperature was observed in rare earth manganite when irradiated with heavy ion (Ogale et al 2000, Ravikumar et al 2004) or substituting transition metal in Mn site (Pen et al 2001) or rare earth in La site (Volkov et al 2007).

### 5.2 ELECTRON SPIN RESONANCE

The method of electron magnetic resonance is an effective tool for probing inhomogeneities in magnetic materials, allowing the determination of the magnetic states of the coexisting phases and their behavior for various temperatures and magnetic fields (Volkov et al 2006). Electron spin resonance (ESR) is expected to be sensitive to measure the magnetic properties of solids. Since this technique requires only a very small amount of powder or crystals, and since temperature dependent measurements are not
time-consuming, it may be convenient to give straightforward information about the various properties related to the many possible ionic combinations relevant in the field. In fact, in the case where one probes the response of an ion that is embedded in the ordered network (as Mn here), the ESR signal in a magnetically ordered phase becomes FMR (ferromagnetic resonance) or AFMR (antiferromagnetic resonance). The relevant parameters governing the corresponding lines are the exchange integral, the magnetic anisotropy and, in the FMR case, the demagnetizing field and the shape of the magnetic domains. This leads to characteristic anisotropy curves describing the line position Vs crystal orientation in the planes among the three possible orientations (easy, intermediate and hard) of the magnetization. In the present case ESR spectrum was measured along the easy axis of magnetization. Moreover, for FMR, the dependence on the domain shape through the demagnetizing field is an additional difficulty.

Electron spin resonance measurements were performed with a Bruker ER 200 ESR spectrometer. The spectrometer, equipped with a temperature-controlled nitrogen-flux cryostat giving access to the temperature range 130–400 K, operates at 9.5 GHz (X-band). The sensitivity of the ESR technique is that a very small amount of powder (= 100 µg) is sufficient. The ESR spectra were recorded upon heating the sample from 200 to 300 K. The rectangular shape single crystals were used for the measurements and c axis of single crystals was aligned perpendicular to the static magnetic field. The temperature dependent ESR spectra of unirradiated and 90 MeV oxygen ion irradiated with fluence of 1x10^{11} ions/cm^2, 1x10^{12} ions/cm^2 and 1x10^{13} ions/cm^2 are shown in Figure 5.1.
Figure 5.1  Temperature dependent ESR spectrum of (a) unirradiated crystal and 90 MeV O ion irradiated with fluence (b) $1 \times 10^{11}$ ions/cm$^2$, (c) $1 \times 10^{12}$ ions/cm$^2$ and (d) $1 \times 10^{13}$ ions/cm$^2$. 
Figure 5.2  Temperature dependent ESR spectrum of (a) unirradiated crystal and 45 MeV Li ion irradiated crystals with fluence (b) $1 \times 10^{12}$ ions/cm$^2$, (c) $1 \times 10^{13}$ ions/cm$^2$ and (d) $5 \times 10^{13}$ ions/cm$^2$. 

\[ \text{Field (mT)} \]
The figure shows the representative ESR spectra in the paramagnetic and ferromagnetic states. A single asymmetric line was observed in the paramagnetic state. There was no change in line shape up to 260 K. The spectrum splits into prominent low-field and high-field ferromagnetic resonance (FMR) lines near the Curie temperature. The unirradiated crystals ESR spectrums are very broad in the low temperature region compared with irradiated crystals except $1 \times 10^{11}$ ions/cm$^2$ fluence. The broadening of spectrum due to ferromagnetic ordering was also observed for $1 \times 10^{11}$ ions/cm$^2$ fluence. Further increase of irradiation fluence $1 \times 10^{12}$ ions/cm$^2$ and $1 \times 10^{13}$ ions/cm$^2$ did not yield broadening. But for the fluence of $1 \times 10^{13}$ ions/cm$^2$ additional peak observed at higher magnetic field region may be due to the additional phase or inhomogeneity (Keon Woo Joh et al 2003).

The temperature dependent 45 MeV Li ion irradiated with fluence $1 \times 10^{12}$ ions/cm$^2$, $1 \times 10^{13}$ ions/cm$^2$ and $5 \times 10^{13}$ ions/cm$^2$ are shown in Figure 5.2. The ESR spectra are broad below the Curie temperature and less broadening for $5 \times 10^{13}$ fluence. For the unirradiated and irradiated with $1 \times 10^{13}$ ions/cm$^2$ and $5 \times 10^{13}$ ions/cm$^2$ fluence, high magnetic field peak moves towards high magnetic field region with decreasing temperature due to influences of localized magnetic moments (Phan et al 2007). Increase in the splitting of the spectrum in the low temperature region clearly indicate the ferromagnetic correlation. The splitting of ferromagnetic resonance has been observed in many rare earth manganite (Angappane et al 2003). At higher fluence of $5 \times 10^{13}$ ions/cm$^2$ such splitting was not observed. The variation in line shape is consistent with magnetization measurements. The lines are well separated below the Curie temperature for lithium ion irradiated crystals compared with oxygen ion irradiated crystals. A shoulder develops on the low-field side of the spectrum, decrease in intensity with decreasing temperature and more broadening especially for lithium ion irradiated crystals than oxygen ion irradiated crystals.
5.2.1 **Heavy Ion Irradiation Effect on g\textsubscript{eff} Parameter**

The temperature dependence of the effective g-value (g\textsubscript{eff}), corresponds to the magnetic field of the maximum microwave absorption. The g\textsubscript{eff} -values above T\textsubscript{c} are not much deviated from that of the free electron value of about 2, which is indicative of paramagnetic nature. On the other hand, the g\textsubscript{eff} exhibits a marked decrease or increase with decreasing temperature below T\textsubscript{c}, corresponding to rapidly growing interactions between the ferromagnetic microregions leading to their alignment in a direction. The temperature dependent variation of g value as a function of 90 MeV oxygen and 45 MeV lithium ion irradiated crystals are shown in the Figures 5.3 and 5.4. In all samples of the present study, the g\textsubscript{eff} value is close to 2 in the paramagnetic region, but showed different behavior in the ferromagnetic region. It has been reported (Oseroff et al 1996, Shengelaya et al 1996) that the g\textsubscript{eff} value remains close to 2 in the paramagnetic region.

Unirradiated crystal showed g\textsubscript{eff} value near to 2 but oxygen ion irradiated crystals showed less than 2 in the ferromagnetic region and increases to 2 in the paramagnetic region. But lithium ion irradiated crystals showed the g\textsubscript{eff} value larger than 2 in the ferromagnetic region and decreases to 2 in the paramagnetic region. Oxygen ion irradiated crystals did not possess the free electron g value and may be due to the ferromagnetic clustering effect in the paramagnetic region. Lithium ion irradiated crystals exhibit a increasing g\textsubscript{eff} value with decreasing temperature below T\textsubscript{c}. This may be due to rapidly growing interactions between the ferromagnetic micro-regions leading to their alignment in a direction (Joh et al 2002).
Figure 5.3  Temperature dependent $g_{\text{eff}}$ value as a function of 90 MeV O ion irradiated crystal with fluence of $1 \times 10^{11}$ ions/cm$^2$, $1 \times 10^{12}$ ions/cm$^2$ and $1 \times 10^{13}$ ions/cm$^2$

Figure 5.4  Temperature dependent $g$ value as a function of 45 MeV Li ion irradiated crystal with fluence of $1 \times 10^{12}$ ions/cm$^2$, $1 \times 10^{13}$ ions/cm$^2$ and $5 \times 10^{13}$ ions/cm$^2$
5.2.2  Line Width as a Function of Irradiation with 90 MeV O and 45 MeV Li Ions

Figures 5.5 and 5.6 show the variation of the line width as a function of irradiated fluence of 90 MeV O and 45 MeV Li ions respectively. In the present study, temperatures of the samples were increased from 200 K to 300 K. Line width of oxygen and lithium ion showed different behavior as shown Figures 5.5 and 5.6. For all the crystals the line width decreases linearly with increasing temperature and showed minimum near to room temperature. In the case of oxygen ion irradiated crystal, ESR line width increases with increasing fluence of $1 \times 10^{11}$ ions/cm$^2$ and $1 \times 10^{12}$ ions/cm$^2$ compared with unirradiated single crystal. Irradiated crystal with fluence of $1 \times 10^{13}$ ions/cm$^2$ showed a decrease in line width compared to unirradiated. In the case of lithium ion irradiated crystals the line width is lower compared with unirradiated crystals. For Li ion fluence value of $1 \times 10^{12}$ ions/cm$^2$ and $1 \times 10^{13}$ ions/cm$^2$ ESR line width decrease and the observed behavior is opposite to oxygen ion irradiated fluence $1 \times 10^{11}$ ions/cm$^2$ and $1 \times 10^{12}$ ions/cm$^2$.

At higher fluence ($5 \times 10^{13}$ ions/cm$^2$) of Li ion, line width increased close to unirradiated crystal compared with lower fluence. As the temperature is lowered below $T_c$, the ferromagnetic micro-regions can be expected to grow into the nearby hole-poor regions, random in their shape and distribution, besides their alignment with each other (Joh et al 2002). In the ferromagnetic region, the ESR line width increases rapidly in the case of oxygen ion compared with lithium ion. This increase may be associated with the critical "slowing down" of the spin fluctuations (Shengelaya et al 1996). It was reported in polycrystalline samples, that the shape of the crystallites is irregular, giving rise to a distribution of the demagnetizing factors which could result in an increase in the line width (Gundakaram et al 1998). Due to the large penetration depth of lithium, more defects were created compared
with oxygen ion. Lithium ion creates more distortion in the Mn-O lattice and weakens the double exchange, which may reduce the line width in the ferromagnetic region. In the case of oxygen ion, increase in line width is due to the enhancement of spin–lattice coupling, which is related to the e_g electron localization concerning small polarons.

**Figure 5.5** Temperature dependent ESR line width as a function of 90 MeV O ion irradiated fluence

**Figure 5.6** Temperature dependent ESR line width as a function of 45 MeV Li ion irradiated fluence
Since the variation in line width around $T_c$ is apparently dominated by exchange-narrowed spin–lattice interactions, the increase of the line width reveals the double exchange interaction to be strengthened and as a result of FM–PM phase transition occurs when the temperature decreases to $T_c$ (Ji et al 1998). Due to ferromagnetic ordering, the local magnetic fields would become more inhomogeneous with lowering the temperature, the ESR line width thus becoming broader.

5.2.3 Temperature Dependent Resonance Field as a Function of 90 MeV O and 45 MeV Li Ion Fluence

The resonance field is determined from the zero crossing point of the ESR spectrum. Temperature dependent resonance field ($H_{reso}$) as a function of 90 MeV O ion irradiated fluence are shown in Figure 5.7. For the initial fluence of $1 \times 10^{11}$ ions/cm$^2$ and $1 \times 10^{12}$ ions/cm$^2$, $H_{reso}$ was increased continuously while decreasing the temperature below the Curie temperature. For fluence of $1 \times 10^{13}$ ions/cm$^2$, $H_{reso}$ was decreased lower than unirradiated crystal and not much variation was observed below the Curie temperature. ESR results were consistent with resistivity and magnetization measurements. The increasing resonance field to higher value may be due to the increase of ferromagnetism and the increase in magnetization was also observed for initial fluence in magnetization measurements. The initial fluence enhance the magnetic property by removing strain in the lattice. Higher fluence creates more distortion and hence decrease the magnetization and the Curie temperature.

Temperature dependent resonance field ($H_{reso}$) as a function of 45 MeV Li ion irradiated for different fluence are shown in Figure 5.8. All the irradiated crystals showed less resonance field ($H_{reso}$) than unirradiated crystal. For the fluence of $1 \times 10^{12}$ ions/cm$^2$, $H_{reso}$ is decreased to low value compared with other crystals. $H_{reso}$ field was increased with increasing fluence.
of $1 \times 10^{13}$ ions/cm$^2$ and $5 \times 10^{13}$ ions/cm$^2$. For higher fluence, $H_{\text{reso}}$ did not reach the value of unirradiated crystals. The decrease of $H_{\text{reso}}$ field to low magnetic field ($H$) regime may be due to some additional structures in the resonance line (Li and Yuan 2004). The additional structure in the resonance line caused the broadening of resonance line.

![Image of Figure 5.7](image1)

**Figure 5.7** Temperature dependent ESR resonance field as a function of 90 MeV O ion irradiated fluence

![Image of Figure 5.8](image2)

**Figure 5.8** Temperature dependent ESR resonance field as a function of 45 MeV Li ion irradiated fluence
5.3 MAGNETIC PROPERTIES OF HEAVY ION IRRADIATED CRYSTALS

5.3.1 Magnetic Properties of 90 MeV O and 45 MeV Li Ions Irradiated Crystals

Measurements of temperature dependent magnetization $M(T)$ were carried out for all the irradiated crystals with zero-field cooling protocols. Figure 5.9 shows the temperature dependent magnetization ($M$) of 90 MeV O ion irradiated LPMO single crystals with 0.05 T field. All samples undergo paramagnetic (PM) to ferromagnetic (FM) transition. Unirradiated single crystal showed the Curie temperature at 252 K and it increases to 256 K for a fluence of $1 \times 10^{11}$ ions/cm$^2$ and $1 \times 10^{12}$ ions/cm$^2$. Further increase in irradiation fluence $1 \times 10^{13}$ ions/cm$^2$ decreased the Curie temperature to 252 K. Meanwhile magnetization is also increased for the fluence of $1 \times 10^{11}$ ions/cm$^2$ and $1 \times 10^{12}$ ions/cm$^2$ weakened for higher fluence of $1 \times 10^{13}$ ions/cm$^2$ irradiated crystal. Similar results were reported for 200 MeV Ag ion irradiated La$_{0.7}$Ce$_{0.3}$MnO$_3$ and 250 MeV Ag ion irradiated La$_{0.7}$Ca$_{0.3}$MnO$_3$ (Ravi Kumar et al 2004, Ogale et al 2000).

Temperature dependent magnetization as a function of 45 MeV Li ion irradiated LPMO single crystals is shown in figure 5.10. The unirradiated and irradiated crystal showed the Curie temperature near to 250 K. For the initial fluence of $1 \times 10^{12}$ ions/cm$^2$, the Curie temperature was increased from 252 K to 256 K and then decreased to 252 K for the fluence of $1 \times 10^{13}$ ions/cm$^2$. Further increase in irradiated fluence, leads to broadening of the Curie temperature between 221 K to 254 K. The Li ion irradiated crystals showed a decrease in magnetization value with increasing irradiation fluence. Magnetization of Li ion irradiated LPMO crystals showed different behavior from oxygen ion irradiated crystals. This may be due to large penetration depth of Li ion. Decrease of magnetization with different irradiated fluence has also been observed in Ag irradiated La$_{0.7}$Ca$_{0.3}$MnO$_3$ rare earth manganite.
(Ogale et al 2000) which is consistent with our result. The reduction in magnetization values indicates that Li ion irradiation produced more distortion in MnO$_3$ octahedral or double exchange mechanism.

![Figure 5.9](image1.png)

**Figure 5.9** Temperature dependent magnetization of LPMO single crystals as a function of 90 MeV O ion irradiated fluence

![Figure 5.10](image2.png)

**Figure 5.10** Temperature dependent magnetization of LPMO single crystals as a function of 45 MeV Li ion irradiated fluence
Figure 5.11 Temperature dependent inverse susceptibility of LPMO single crystals as a function of 90 MeV O ion irradiated fluence

Figure 5.12 Temperature dependent inverse susceptibility of LPMO single crystals as a function of 45 MeV Li ion irradiated fluence
The inverse susceptibility showed a linear dependence with temperature in the range 260–300 K, below which a deviation occurs. In the high-temperature region (above \( T_c \)) the magnetic susceptibility was fitted to the Curie–Weiss law. Figure 5.11 shows the inverse magnetic susceptibility for 90 MeV O ion irradiated LPMO single crystals. At elevated temperatures all susceptibility follow the Curie-Weiss (CW) law. The Curie constant (\( \Theta \)) increases from 262 K (unirradiated crystal) to 265 K for \( 1 \times 10^{11} \) ions/cm\(^2\) fluence. It decreases to 263 K and 262 K for \( 1 \times 10^{12} \) and \( 1 \times 10^{13} \) fluence. The increase in Curie constant (\( \Theta \)) indicates that the ferromagnetic clustering in paramagnetic region is increased due to the increasing ferromagnetic correlation between Mn\(^{3+} \) and Mn\(^{4+} \) ions. Figure 5.12 shows the inverse susceptibility for 45 MeV Li ion irradiated LPMO single crystals and follow the Curie-Weiss law at high temperature.

The Curie constant (\( \Theta \)) (262 K) is similar for unirradiated and irradiated (\( 1 \times 10^{12} \) ions/cm\(^2\)) fluence. For the fluence of \( 1 \times 10^{13} \) ions/cm\(^2\) and \( 5 \times 10^{13} \) ions/cm\(^2\) the Curie constant is decreased to 261 K and 257 K respectively. The formation of ferromagnetic clusters causes a deviation from Curie-Weiss law starting at 260 K. Such cluster formation though rare in conventional manganites is reported in La\(_{2/3}\)Ca\(_{1/3}\)MnO\(_3\) around 20 K above its \( T_c \) (Amaral et al 1998) and at higher fields the cluster formation gets suppressed. The Curie constant is decreased continuously for lithium ion irradiation and in the case of oxygen ion irradiation it increased initially and then decreased. This may be due to the distortion in the Mn-O octahedral produced by the ion, which modified the double exchange between Mn ions. It is evident from the figure that there is a deviation from Curie–Weiss behavior in the paramagnetic region for all these samples. This suggests the presence of magnetic inhomogeneties in the paramagnetic region (Rana et al 2004).
5.3.2 ZFC and FC Magnetization Properties of Irradiated Crystals

The field cooled (FC) and zero field cooled (ZFC) magnetization measurements were performed in low applied magnetic field of 2 mT. ZFC and FC magnetization results of unirradiated and 90 MeV oxygen ion irradiated (1x10^{13} ions/cm^2 fluence) LPMO single crystals are presented in Figure 5.12.

It is observed that at low temperatures, the FC and ZFC magnetization curves are separated from each other and the samples behave spin-glass-like manganites. The ferromagnetic-to-paramagnetic transition temperature, T_c was estimated for these two samples near to 252 K. The deviation between ZFC and FC magnetization is similar for both samples and not much difference is observed. It is expected that heavy ion irradiation creates distortion in the oxygen site and may increase the cluster glass behavior. From the above measurement, the cluster glass property of oxygen ion irradiated crystal is not modified. ZFC and FC magnetization results of unirradiated and 45 MeV Li ion irradiated with 5x10^{13} fluence are shown in Figure 5.13. The transition temperature of both unirradiated and 5x10^{13} fluence irradiated crystals are same and with a small difference in magnetization value. The bifurcation between ZFC and FC was increased in lithium ion irradiated crystals compared with unirradiated crystals. From the figure it is clearly seen that the cluster glass property of the irradiated crystals was increased.
Figure 5.13 Temperature dependent low field ZFC and FC magnetization of unirradiated and 90 MeV O ion irradiated (fluence of $1 \times 10^{13}$ ions/cm$^2$) LPMO crystals

Figure 5.14 Temperature dependent low field ZFC and FC magnetization of unirradiated and 45 MeV Li ion irradiated (fluence of $5 \times 10^{13}$ ions/cm$^2$) LPMO crystals
5.4 CONCLUSION

Heavy ion irradiated LPMO single crystals have been studied by ESR and magnetization measurements. Temperature dependent ESR measurements of irradiated crystals clearly indicate the changes in the magnetic properties as function of irradiated fluence. g parameter of oxygen ion irradiated crystals showed higher value than lithium ion irradiated crystal, which may be due to the increase of inhomogeneity of the crystal. Increasing inhomogeneity or cluster glass property in lithium doped crystal was confirmed by ZFC and FC magnetization measurements. $H_{\text{reso}}$ showed different behavior for oxygen and lithium ion irradiated crystals. The decrease of $H_{\text{reso}}$ was observed for lithium ion crystals due to additional magnetic phase formed in the crystals. Increase in ESR line width was observed for oxygen ion due to ferromagnetic correlation and decreased for lithium ion irradiation. Magnetization measurement of oxygen ion irradiated crystal increased lower fluence ($1 \times 10^{11}$ ions/cm$^2$) and then decreased for the fluence of $1 \times 10^{13}$ ions/cm$^2$. Li ion irradiated crystals showed decrease in magnetization with increase of the Curie temperature for initial fluence and then decreases for higher fluence. Inverse magnetic susceptibility clearly indicates the decrease of ferromagnetic clustering in the paramagnetic region with lithium ion irradiation.