CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

6.1 SUMMARY

La$_{1-x}$Pb$_x$MnO$_3$ (0<x<1) is an interesting system due to its large magneto-resistance ratio and the Curie temperature near to room temperature. The preparation of good quality crystal with uniform composition of lead and oxygen are very important for large magnetoresistance ratio. This system has been studied mostly at Pb = 0.3 due to crossover from semiconductor to metal transition at room temperature. Most of the colossal magneto-resistance materials are synthesized around 1573 K due to increase in the reaction of oxide material, but Pb based materials are synthesized below 1573 K due to the low melting point and easy evaporation of Pb at high temperature. Evaporation and contamination of lead flux is a serious problem in lead based crystal growth. To avoid the evaporation of lead, we added 5 weight percentage of B$_2$O$_3$ with flux because B$_2$O$_3$ is more viscous and might reduce the evaporation of lead. Optimized growth temperature from 1323 K to 1223 K was used for the growth of the crystals. Single crystals of size 1×0.5×0.5 mm$^3$ were obtained for the flux-charge ratio of 5:1 due to high evaporation of flux and it was difficult to maintain the Pb content. Maximum crystal size of 5×4×3 mm$^3$ was obtained for the flux-charge ratio of 6:1.

The grown crystals exhibit layer growth and hopper growth pattern. The layer pattern depends on different growth conditions such as temperature fluctuation and supersaturation of liquid phase. The step growth process is dominant when the supersaturation level is moderate and hopper growth
pattern due to the latent dissipation was more rapid at the corners than at the centre of faces. The structural parameters were estimated by refining the powder XRD pattern using the MAUD program and refined lattice parameter values are \( a = b = 5.5285(1) \text{ Å} \), \( c = 13.4180(3) \text{ Å} \). The back reflection Laue pattern shows ab plane of trigonal lattice and clear reflection spots without shadow confirms the good quality of the crystals. The composition of the crystals measured using EDX was found to be \( \text{La}_{0.91}:\text{Pb}_{0.09}:\text{Mn}_{1} (\pm 5\%) \). EDX measurement shows uncertainty due to overlapping of La L edge and Mn K edge.

In the absence of the magnetic field, the temperature dependent resistivity (\( \rho \)) showed metal insulator transition temperature (\( T_{\text{MI}} \)) at 247 K. The temperature dependent resistivity was also studied with 6 T field. The applied field of 6 T raises the \( T_{\text{MI}} \) from 247 K to 306 K and suppresses the resistivity peak and thus yielding a large magneto-resistance near the Curie temperatures. The resistivity at 250 K drops by \( 5 \times 10^4 \) times with the application of 6 T field. The observed CMR (99.5\%) was higher than the reported value for \( \text{LaPbMnO}_3 \) system. The mechanism of CMR is not necessarily associated with the FM phase and extremely large CMR emerges near the Curie temperature as the external field induces spin flopping in the AFM state. Activation energies (\( E_{\text{P}} \)) have been estimated and are found to be \( \sim 70 \text{ meV} \) and decreases with increasing magnetic field and the observed behavior may be due to the localization of charge carriers in the presence of magnetic field.

The X-ray photoelectron spectroscopy studies confirmed the binding energy of La 3d, Mn 2p, Pb 4f and O 1s core levels. From the hysteresis measurement it was observed that the easy axis of magnetization along the ab plane of the single crystal and all the measurements were carried out along ab plane. Zero field cooled (ZFC) and field cooled (FC)
magnetization measurements were carried out to study the cluster glass properties of LPMO single crystals at 2 mT and 0.05 T magnetic field. Low field ZFC and FC measurements confirmed the cluster glass property and was removed by 0.05 T field. Ferromagnetic spin clustering effect in the paramagnetic region was observed and starts at the temperature near to 1.03 Tc and 1.04 Tc. Near Tc the electron spin resonance (ESR) spectrum split into prominent low field and high field ferromagnetic resonance line. The lines are very well separated and the low field side started to increase with the decreasing temperature, which corresponds to more inhomogeneous local magnetic field distribution.

The 90 MeV O and 45 MeV Li ion irradiated single crystals showed surface modification as a function of fluence and more surface damage was observed for oxygen ion irradiation. The estimated range of 90 MeV oxygen ions and 45 MeV Li ions in LPMO thin films is 77 µm and 219 µm, respectively and lithium ion produced extend defects. Temperature dependent resistivity showed increase in TMH and resistivity for initial fluence and decreased TMH with increase of fluence due to the relaxation of strain. Li ion irradiation increased the low temperature colossal magnetoresistance compared with oxygen ion, which may be due to the defect or grain boundary contribution. Magnetization increases with increase of Tc for oxygen ion irradiation and decreases in magnetization for 1x10^{13} ions/cm² fluence. But lithium ion irradiation showed decrease in magnetization for all crystals due to more distortion or defect extended to larger thickness. Lithium ion irradiation increased cluster property of the 5x10^{13} ions/cm² irradiated crystals. Temperature dependent ESR measurement clearly indicate the increase of ferromagnetism for initial fluence by splitting of ESR spectrum. The $g_{\text{eff}}$, ESR line width and resonance field showed opposite behavior for lithium and oxygen ion. The results clearly indicate the extended defect produced longer thickness by lithium and oxygen ion produce over larger
more surface defects. The colossal magnetoresistance and magnetic transition temperature were modified with heavy ion produced controlled defects in the materials.

6.2 SUGGESTIONS FOR FUTURE WORK

In order to study the composition dependent colossal magnetoresistance properties of LPMO single crystals, good quality single crystals with uniform composition is very important. Still there is no report available for single crystals of La$_{1-x}$Pb$_x$MnO$_3$ for 0<x<1. Single crystal growth method may be modified to avoid the large variation of flux material and correct weight percentage of B$_2$O$_3$ should be optimized.

Size mismatch will reduced by choosing correct divalent or trivalent ion to modify the A site cation size in the perovskite structure. Correct tuning of the cation radius will give large magnetoresistance above room temperature.

To study the irradiation effect, good quality single crystals with thickness lower than the projected range are essential. The lighter and heavier ion irradiation may be attempted to modify the transport and magnetic properties of LPMO crystals.