CHAPTER 2

GROWTH, STRUCTURAL, SURFACE MORPHOLOGY
AND TRANSPORT PROPERTIES OF
LaPbMnO₃ SINGLE CRYSTALS

2.1 INTRODUCTION

The broad features of the mixed-valence manganese perovskites were described for many polycrystalline ceramic samples (Jonker and van Santen 1950). In early 1950’s the preparation, crystal structure and magnetic properties of the (La₁₋ₓCaₓ)MnO₃ series (Jonker and van Santen 1950) and a short account of the electrical resistivity (van Santen and Jonker 1950) were discussed. Similar results were observed for the (La₁₋ₓSrₓ)MnO₃ and (La₁₋ₓBaₓ)MnO₃ series but the range of solid solution was limited to x < 0.7 or x < 0.5 respectively. Magneto-resistance and other transport properties were first described by Volger et al (1954) who showed that the magneto-resistance of (La₀.₈Sr₀.₂)MnO₃ is negative with a peak near the Curie temperature. An extensive study of flux-grown single crystals of (La₁₋ₓPbₓ)MnO₃ with 0.2 < x < 0.44 was carried out (Searle and Wang 1969, Morrish et al 1969).

The metallic conductivity below the Curie point Tₛ and a large negative magneto-resistance effect of about 20 % at 1 T in the vicinity of Tₛ were observed. The growth and magnetic properties of La₁₋ₓPbₓMnO₃ (LPMO) crystal have been reported by Morish et al (1969). The theoretical calculation based on the Kondo-lattice model with ferromagnetic coupling has been presented by Kubo and Ohata (1972), which could give an essential
account for the large MR observed near the Curie temperature $T_c$. The Jahn-Teller effect and electron phonon coupling have been proved by optical measurement on La$_{0.7}$Pb$_{0.3}$MnO$_3$ single crystals (Litvinchuk et al 2000) and positron annihilation studies on LaPbMnO$_3$ poly crystals (Banerjee et al 2001). Perrig et al (1996) reported the existence of magnon in LPMO with an energy of 95 MeV by inelastic neutron experiment.

2.2 PROPERTIES OF LaPbMnO$_3$

Among CMR materials investigated, two systems of Sr and Pb doped La$_{1-x}$(Sr, Pb)$_x$MnO$_3$ manganites have the highest $T_c$ values. This was explained in detail by Radaelli et al (1997). CMR effect near 300 K was observed in these materials (Searle and Wang 1970). X-ray and ultraviolet photoemission based experiments revealed an existence of the double-exchange conduction band in the FM regime $T < T_c$ (Alvarado et al 1976). However, previous works did not on the wide range and only investigated on a narrow range of the $x$ value. The properties of La$_{1-x}$Pb$_x$MnO$_3$ compounds with a wide doping range of $0.1 \leq x \leq 0.5$ was investigated by Mahendiran et al (1995). It was shown that $T_c$ of the samples investigated was between 300 K and 340 K. At a relatively low doping level ($x = 0.1$) the CMR value at 300 K was 80 % at 6 T. At the same time Jia et al (1995) also reported that CMR of a La$_{0.6}$Pb$_{0.4}$MnO$_3$ single crystal reached a maximum value of 64 % at 6 T.

Perovskite manganite doped with Pb (La$_{1-x}$Pb$_x$MnO$_3$) has been studied due to the significant electrical and magnetic properties of this materials family (Chau 2003). It is interesting that La$_{1-x}$Pb$_x$MnO$_3$ ($0.1 \leq x \leq 0.5$) compounds with their $T_c$ values around 300 K have potentials for high-temperature applications (Jia et al 1995). Magnetic tunnel junctions have been fabricated using Pb doped manganite films by Yamada et al (2002). CMR effects are strongest in the region $0.15 < x < 0.5$ for most Ln$_{1-x}$A$_x$MnO$_3$ system, however LPMO exhibit CMR from $x = 0.1$ to 0.5. A large variation of $T_c$ values for LPMO ranging from 250 K to 350 K has been reported in the
Controversy between the reports for the $T_c$ of the samples is due to the quality and preparation of the samples. The polycrystalline manganites are of special interest as their synthesis procedure is much faster and easier compared to the single crystals. They are widely used for thin film preparation as targets for laser ablation and magnetron sputtering. The available experimental $T_c$ values and magnetoresistance compiled by Vladimirova et al (2001) was shown in Figures 2.1 and 2.2.

Figure 2.1 Comparison of the Curie temperatures for La$_{1-x}$Pb$_x$MnO$_3$ manganites. Opened symbols-polycrystalline samples, filled symbols- single crystals. Solid line –results of the Vladimirova et al (2001)

For single crystals the difference between $T_c$ values is 14 K while for polycrystalline samples, it is slightly higher about 20 K (Vladimirova et al 2001). The general tendency is the gradual increase of $T_c$ with x, which is more pronounced in single crystalline samples. It should be pointed out that $T_c$ values for polycrystalline samples with $x = 0.26$ (Sahana et al 1997) and
0.33 (Booth et al. 1996) are lower than 300 K. The large spread of $T_c$ values for polycrystalline samples as compared to the single crystals of the same composition, indicate the peculiarities of synthesis and annealing of LaPbMnO$_3$ manganite.

Figure 2.2  Pb substitution concentration dependent of the low-field magneto-resistance and saturation magnetization $M_{sat}$ at 5 K (Vladimirova et al. (2001))

2.3 EXPERIMENT

La$_{1-x}$Pb$_x$MnO$_3$ (LPMO) system has been studied mostly at Pb = 0.3 due to the crossover from semiconductor to metal transition at room temperature. Growth of Pb doped rare earth manganite single crystals has been reported (Lin et al. 1999, Nilotpal Ghosh et al. 2005a) but very less work has been reported on LPMO single crystals at Pb = 0.1. Flux growth method is one of the most commonly used processes to produce single crystals in the case of incongruent melting systems. Growth of high quality and large single crystals of rare earth manganite using various flux methods and floating zone
method have been carried out (Prabhakaran and Boothroyd 2002, Vogel et al 1975). Most of the colossal magneto-resistance materials are synthesized around 1573 K due the reaction of oxide material. But Pb based material is synthesized below 1573 K due to the low melting point and easy evaporation of Pb at high temperature. The eutectic composition of PbO-PbF$_2$ is 1:1.17, which gives low melting point of flux and complete dissolution of charge at low temperatures (Nilotpal Ghosh et al 2005a).

2.3.1 Crystal Growth Apparatus

A resistive heating furnace used for the crystal growth is shown in Figure 2.3. Kanthal wire heating elements are more suitable when prolonged heating is necessary in the range up to 1373 K. The core tube of pure alumina was wound by kanthal wire and mounted vertically on a firebrick base. Corundum powder was applied in between wounded kanthal wire to prevent the short circuit. This set up is completely surrounded with highly insulating glass wool and then with firebrick so that the only opening to the furnace is from the top. A stand made of firebrick was placed inside the core tube to support the crucible in the hot zone of the furnace. After the crucible was placed in the furnace, the top was plugged with firebrick. An exhaust fan was mounted in the side of the wall to let out the poisonous nature of the lead vapors, which otherwise would go-off into the room. The permitted cooling rate was as low as 1 K/h.

In practice, crucible selection for high temperature solution growth technique is a matter of convenience, economic and trial and error. However, the experience of many workers has distilled into certain guidelines. Metals are usually grown mostly from crucibles that are covalent or ionic such as fused silver or Al$_2$O$_3$. Ionic materials are usually grown from metallic crucibles. Elwell and Scheel (1975) presented together with the noble metals, a list of other crucible materials such as silica glass, graphite, nickel, molybdenum and tantalum. In most cases a reducing or at least an inert
atmosphere has to be used. In the flux growth method platinum has been found widely used as a container material for most of the oxides because of its high melting point and high resistance at necessary atmosphere. Despite its high cost and softness, pure platinum is more resistant to attack by fluxes and recommended for rhodium doping. Since this material is rather soft at high temperature, it is very useful if embedded in refractory materials. A few flux systems containing Pb ion attack the crucible severely and form an intermetallic compound. Graphite or vitreous carbon serves as an excellent crucible for many metals and ionic halides. In the present investigation, rhodium doped platinum crucibles have been used in all growth experiments.

1. Outer Chamber, 2. Insulating material, 
3. Refractory tube, 4. Heating element 
5. Thermocouple, 6. Alumina crucible, 7. Platinum foil, 
8. Platinum crucible, 9. Crucible stand

Figure 2.3 Schematic diagram of crystal growth furnace used for the growth of LPMO single crystals.
2.4 CRYSTAL GROWTH

The traditional synthesis of rare earth manganites by solid state or ceramic route involves the high-temperature (1373 K - 1573 K) annealing of the carbonates or oxides mixtures in a controlled atmosphere. Meanwhile, it is well known that the lead oxides starts to melt at 1163 K and evaporates as Pb$_2$O$_2$ and Pb$_4$O$_4$ (Valdimirova et al 2001) upon further increase of temperature. To reduce the lead evaporation maximum temperature of 1323 K was used for the synthesis and the growth of crystal. Initially, polycrystals of La$_{0.9}$Pb$_{0.1}$MnO$_3$ were prepared by the solid state reaction method. Stoichiometric amount of La$_2$O$_3$, PbO and MnO$_2$ powders were homogeneously mixed. Then the mixed powder was sintered at 1073 K for 24 h and kept at 1273 K for 24 h with intermediate grinding. It is reported that Pb substituted LaPbMnO$_3$ single phase perovskites were obtained below x < 0.4 and doping at Pb x > 0.4 showed secondary phase Pb$_3$Mn$_6$O$_{13}$ (Shamesh et al 1998).

After synthesis, LPMO powder was mixed with flux material in two different precursor ratios. The different flux with precursor ratio (5:1 and 6:1) was used to study the crystal quality. 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. For the growth process PbO-PbF$_2$ was used in 1:1.15 ratio. The mixture of flux and precursor were transferred to a platinum crucible and covered with a platinum foil. Then the crucible was inserted in an alumina crucible and covered using an alumina lid. To reduce the Pb evaporation, aluminum paste was used for tightening the lid. The alumina crucible was placed in a resistive heating vertical single zone furnace attached with Eurotherm controller. The furnace had 7 cm homogeneous temperature zone and the whole crucible was kept in constant temperature region during growth.
Figure 2.4 Photograph of the crucible after the crystal growth and crystals are formed near the crucible wall

Figure 2.5 Thermal cycle used for the growth of LPMO crystals
The content of Pb and the size of the crystals decreased with a higher growth temperature (1573 K) for the same initial flux composition and at the same cooling rate. The growth of the crystal was terminated at around 1223 K (Lin et al 1999). Optimized growth temperature from 1323 K to 1223 K was used for the growth of the crystals. During the heating cycle from room temperature, the temperature was allowed to remain at 673 K for 5 h in order to create an oxygen ambient to reduce the risk of crucible corrosion. At this temperature PbO was transformed to less corrosive Pb$_3$O$_4$, which decomposes by releasing oxygen at higher temperature (Nilotpal Ghosh et al 2005a). Then the temperature was increased to 1323 K at the rate of 50 K/h and soaked for 24 h to get homogenized solution. The furnace was then cooled to 1223 K at the rate of 0.5 K/h.

The temperature was maintained at 1223 K for 12 h in order to evaporate the remaining flux and finally the crucible was quenched to room temperature. Figure 2.4 shows the photograph of the crucible after the growth, which contains the mixture of crystals and flux material. The thermal cycle used for the growth of crystals is shown in Figure 2.5. The single crystals of size 1×1×0.5 mm$^3$ were obtained using the flux: charge ratio of 5:1. Maximum size of 5×4×3 mm$^3$ single crystals were obtained using the ratio of 6:1. The crystals were separated mechanically using hot acetic acid. Crystals grown from different flux with charge ratio is shown in Figure 2.6. The harvested crystals posses cubic and rectangular like morphology.
Figure 2.6 $\text{La}_{0.9}\text{Pb}_{0.1}\text{MnO}_3$ single crystals grown using flux - precursor 6:1 (a) and 5:1 (b).

Figure 2.7 $\text{LaPbMnO}_3$ single crystals separated from the crucible.
2.5 SURFACE MORPHOLOGY

Solution grown crystals develop well-defined morphology, characteristic of the internal symmetry of the crystals. Morphology of bulk single crystals provides more information about habitual faces and growth rates. The information obtained from such studies can be used to improve the growth conditions to obtain better quality crystals. There is no Pt inclusion observed in the crystals during the growth. Crystals start to nucleate at the surface of the melt during slow cooling. After a critical size the crystals start to deposit at the bottom of the crucible. As a result strain is induced in the crystals formed at the bottom of the crucible. On the top, crystals formed around the wall of the crucible have an irregular morphology. At the bottom of the crucible, cubic and rectangular shaped crystals were formed and individual crystals were separated with dimension varying from 1 mm to 5 mm.

Figure 2.7 shows the LPMO crystals obtained from bottom of the crucible. A slight temperature gradient at the bottom of the crucible may initiate supersaturation, which is likely to be followed by the growth of crystals. Crystals found at the top of the surface near to the wall exhibit layer growth pattern and as shown in the Figure 2.8. Evaporation of flux causes an increase in supersaturation near the surfaces. In three dimensional morphology of the crystals, the mechanism of step growth generation is initiated by 2D nucleation followed by subsequent step propagation (Chernov 1984). The step growth process is dominant when the supersaturation level is moderate (Nilotpal Ghosh et al 2005b). The layer pattern depends on different growth conditions such as temperature fluctuation, supersaturation of liquid phase, etc. In some cubic-shaped crystals, the face appeared hollow because the latent dissipation was more rapid at the corners than at the centre of faces.
Figure 2.8 SEM image shows 2D layer growth pattern on the flux grown $\text{La}_{0.9}\text{Pb}_{0.1}\text{MnO}_3$ single crystals

Figure 2.9 Hopper growth pattern observed on $\text{La}_{0.9}\text{Pb}_{0.1}\text{MnO}_3$ single crystals
If the growth is entirely controlled by diffusion, the crystal should take a spherical form with no flat faces. The appearance of flat crystal faces was accounted for by the introduction of the concept of the layer-by-layer growth mechanism on a smooth interface. The driving force over a crystal face is higher at the corners or on the edges than on the face, with a minimum at the center of the face. There is a critical value for two-dimensional nucleation to occur. If the driving force at the corners and edges is lower than this critical value, the growth of this face will be controlled by the spiral growth mechanism. Then the growth layer originating from screw dislocations in the central area of the face will advance outward. So the polyhedral stability of the morphology can be maintained. If the bulk driving force increases above the critical value for two-dimensional nucleation to take place at the corners or edges, dislocations outcropping near the edges or two-dimensional nucleation in these places will act as sources for growth layers and then advance inwards to the central area of the face. This corresponds to the formation of a hopper face as shown in Figure 2.9. If the driving force increases further, three-dimensional nucleation will take place at sites, where the driving force is maximum, namely at the corners of the crystal (Sunagawa 1987).

2.6 POWDER X-RAY DIFFRACTION STUDIES

Figure 2.10 shows XRD pattern of \( \text{La}_{0.9}\text{Pb}_{0.1}\text{MnO}_3 \) single crystals grown in different flux - charge ratio and the reflections are indexed with corresponding hkl values. The powder X-ray diffraction pattern indicates that the crystal is in trigonal structure with \( \text{R}\bar{3}\text{C} \) space group, in which La/Pb are at 6a (0, 0, 1/4) positions, Mn at 6b (0, 0, 1/2) and O at 18e (x, 0, 1/4) position. The structural parameters were obtained by refining the XRD pattern using the MAUD program, which combines the Rietveld method and the Fourier transform analysis in the presence of broadened Bragg peaks (Lutteroti 2000).
Figure 2.10 Powder X-ray diffraction pattern of polycrystal LPMO and single crystals of La$_{0.9}$Pb$_{0.1}$MnO$_3$ grown for different flux-charge ratio

The refined lattice parameter values were $a = b = 5.5285(1)$ Å, $c =$13.4180(3) Å. The structural parameters obtained agree with the reported value (Huang et al 2001). The respective residuals were $\text{Sig} = 1.2$, $R_w (%) = 10.95$, $R_{\text{int}} (%) = 0.10$, $R_b (%) = 8.62$, $R_{\text{exp}} (%) = 8$. Refinement results shows $\approx$ 1 % of PbO impurity and this may be due to the flux material
deposited on the surface of the as-grown single crystals after growth. The weight fraction of LPMO and PbO estimated from the refinements were 0.9885 and 0.0115 (Massicot-Pb ore).

Figure 2.11 Rietveld plot of powder XRD data for LPMO single crystals

Figure 2.11 shows the Rietveld plot of powder XRD data for LPMO single crystals at room temperature. The mark in the picture indicates the position of allowed Bragg reflections of PbO and LPMO. The line curve at the bottom gives the difference between the observed and the calculated values. The structural refinement revealed the presence of a small amount of PbO in the powdered crystal and this was reduced by using a properly cleaned single crystal. Grown crystals are thoroughly cleaned with diluted HCl to remove the Pb on the surface of the crystals. The presence of lead oxide could not be detected through thermal, transport and magnetic property studies.
Hence the flux material was observed only on the surface of the crystals and not as impurity in the crystal lattice.

2.7 LAUE BACK REFLECTION MEASUREMENT

The Laue method is mainly used to determine the orientation of large single crystals. There are two practical variants of the Laue method, the back-reflection and the transmission Laue method. In the back-reflection method the film is placed between the x-ray source and the crystal. The beams, which are diffracted in a backward direction are recorded. One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone with the diffraction spots generally lying on an hyperbola. In the transmission Laue method the film is placed behind the crystal to record beams, which are transmitted through the crystal.

Figure 2.12 Back reflected Laue pattern of LPMO single crystal
Back reflection Laue pattern was recorded using Mo X-ray radiation and the distance between sample and the source was kept at 3cm. The sample was irradiated with X-ray for about 3 h. The back reflection Laue photograph shows ‘ab’ plane of trigonal lattice and clear reflection spots with no shadows confirm the good quality of the crystals. The Laue photograph of the single crystals is shown in Figure 2.12.

2.8 COMPOSITION ANALYSIS

Energy dispersive X-ray analysis (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. In this technique the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. Composition of the single crystals is measured at different parts of the crystals and final composition taken as an average value. The composition of Pb and oxygen play a major role to determine $T_c$ and resistivity of the manganite. The composition of the crystals measured using EDX was found to be $La_{0.91}Pb_{0.09}Mn_1$ (±5%). EDX measurement shows uncertainty due to overlapping of La L edge and Mn K edge. It is difficult to measure correct
oxygen composition using EDX measurement. Figure 2.13 shows the EDX spectrum of LPMO single crystal.

![Figure 2.13 EDX spectrum of LPMO single crystal](image)

2.9 TRANSPORT MEASUREMENT

2.9.1 Temperature and Magnetic Field Dependent Resistivity

A four point probe is a simple method for measuring the resistivity of semiconductor samples. By passing a current through two outer probes and measuring the voltage through the inner probes allows the measurement of the single crystal resistivity. The rectangular shaped single crystals were used to determine the phase transition i.e. metal insulator transition temperature $T_{\text{MI}}$. This measurement involves the transition from metallic to insulating phase of the material. The measurements were carried out in zero field ($H = 0$) and with field (6 T) in the temperature range of 10 K to 350 K with a constant current of 0.001mA. The sample was placed on the sample holder and the silver paint was used to establish contact between the copper wires.
The quantum design physical property measurement system was used for these measurements. It was observed that the resistivity increases with decreasing temperature up to $T_{\text{MI}}$ and then decreases with further decrease in temperature below $T_{\text{MI}}$. It is well known that the transport properties of these materials exhibit a transition from a paramagnetic insulating state to a ferromagnetic metallic state as the temperature is lowered and that the Curie temperature $T_c$ is very close to $T_{\text{MI}}$. The sample shows broad peaks around their respective insulator-metal transitions temperature ($T_{\text{MI}}$) around 247 K. The collapse of electrical resistivity below $T_c$ is an evidence that there is a strong interaction between charge carrier and magnetic moment. In the absence of the magnetic field, the resistivity ($\rho$) has a peak around $T_c$ (252 K). The temperature dependence of resistivity was 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 temperature. Figure 2.14 shows that the temperature dependent resistivity measured in the 0 T and 6 T field for the LPMO single crystal. With the application of a magnetic field (6 T), the character of the phase transition gradually changes.

This feature may be explained by the conventional lattice-irrelevant mechanism, i.e the spin scattering reduced by an external magnetic field. This behavior is typically seen in related CMR perovskite (Bahadur et al 1996). The field-induced drop in resistance was observed immediately following the $T_c$. The application of the magnetic field (B), causes the local ordering of magnetic spin. Due to this ordering, the ferromagnetic metallic (FMM) state suppresses the paramagnetic insulating (PMI) state and hence, the peak temperature ($T_{\text{P}}$) shifts to the high temperature regime with the application of the magnetic field. The semiconducting feature for $T > T_c$ diminishes sharply with an increase in the magnetic field.
2.9.2 Colossal magnetoresistance ratio

Magnetoresistance is the relative change in the electrical resistance or resistivity of a material produced on the application of a magnetic field. It is generally defined by:

$$\text{MR(\%)} = \frac{\Delta R}{R_0} = \frac{R_H - R_0}{R_0} \times 100$$ (2.1)

The MR (%) has also been identified by Eschenfelder (1981) as:

$$\frac{\Delta R}{R_H} = \frac{R_0 - R_H}{R_H} \times 100$$ (2.2)
where $R_H$ and $R_O$ are the resistance at a given temperature in the presence and absence of a magnetic field $H$ respectively (This means that decreasing resistance with magnetic field implies a negative MR). MR can be negative or positive and most metals show a small MR (only a few percent). In non-magnetic pure metals and alloys MR is generally positive and MR shows a quadratic dependence on $H$. MR can be negative in magnetic materials because of the suppression of spin disorder by the magnetic field (Rao and Raveau 1998).

An applied magnetic field ($H$) suppresses the resistivity and thus leads to a negative CMR, the maximum CMR occurs around $T_c$ under a magnetic field of $H = 6$ T as shown in the Figure 2.15. The resistivity at 250 K drops by 500000 times under the application of the 6 T field. The observed CMR was higher than the reported value for LaPbMnO$_3$ system (Jia et al 1995, ghivelder et al 2001) and CMR ratio of 99 % was observed and shown in the inset of the Figure 2.15. The applied magnetic field tends to align the spin direction and promotes the conductivity and leads to CMR. Large CMR is observed in the area, where magnetic inhomogeneity are realized due to the change in relative volumes of the minority and majority phases with different conductivity in the external magnetic field (Volkov et al 2007). At low doping levels, for example $x= 0.1$ to 0.15 composition the experimental results can be interpreted only within the framework of the mixed ferromagnetic – antiferromagnetic ground state model (Vladimirova et al 2001) assuming the presence of ferromagnetic clusters in the non-ferromagnetic matrix (magnetic phase separation). The mechanism of CMR is not necessarily associated with the FM phase and extremely large CMR emerges near the Curie temperature appears as the external field induces spin flopping in the AFM state (Gong et al 1995).
Figure 2.15  Temperature dependence of magnetoresistance ratio ($\frac{\Delta R}{R_0}$) of $\text{La}_{0.9}\text{Pb}_{0.1}\text{MnO}_3$ single crystal. Inset shows the temperature dependence of magneto-resistance ratio ($\frac{\Delta R}{R_0}$)

The delicate nature of the magnetic microstructure in the mixed phase state of hole doped manganites is responsible for the CMR effect in which significant conduction paths are formed between the ferromagnetic domains by the application of magnetic field (Murakami et al 2003).

2.9.3 Conductivity Mechanism Below and Above the Curie temperature

In order to understand the complex conduction mechanism and the relative strengths of various scattering mechanisms at low temperature i.e., in the temperature range from metallic to insulating state and an attempt has been made to fit the resistivity data to various empirical equations.
In the above equations, $\rho_g$ term arises due to the grain/domain boundary. On the other hand, $\rho_e T^2$ term in equations 2.2 and 2.3 represents the resistivity due to electron–electron scattering process, while the term $\rho_{2.5} T^{2.5}$ represents resistivity due to single magnon scattering process in ferromagnetic phase. Finally the term $\rho_{4.5} T^{4.5}$ was attributed to two magnon scattering process in the ferromagnetic region (Venkataiah and Venugopal Reddy 2005). Actually, it is assumed that the later process is more favorable in half-metallic band structure materials such as manganites. The high temperature ($T>T_p$) electrical resistivity has been fitted to two different models in different temperature regions.

In order to explain the electrical conduction just above $T_p$, i.e., $T_p < T < \theta_D/2$, ($\theta_D$ is Debye’s temperature) variable range hopping (VRH) model (Viret 1997) has been used, while adiabatic small polaron hopping (SPH) model (Mott 1971) is considered at temperatures beyond $\theta_D/2$. Typical plots corresponding to small polaron hopping models is shown in Figure 2.16. Further in the temperature region $T>\theta_D/2$, the resistivity data have been fitted to SPH model and from the fitting parameters, activation energies ($E_P$) have been estimated and are found to be 70 meV, which is lower than the values reported earlier (Chattopadhyay et al 2004). It is interesting to note that $E_P$ values are decreasing with increasing magnetic field and the observed behavior may be due to the localization of charge carriers in the presence of magnetic field.
Figure 2.16 Variation of $\ln(\rho/T)$ as a function of inverse temperature (1/T) of $\text{La}_{0.9}\text{Pb}_{0.1}\text{MnO}_3$ with 0 field. The insets represent the data measured in the presence of magnetic field $B = 6$ T. Solid lines are the best fit to Mott’s SPH model.

2.10 CONCLUSION

Single crystals of $\text{La}_{0.9}\text{Pb}_{0.1}\text{MnO}_3$ have been grown by the flux growth technique. The composition was measured quantitatively by EDX studies. Bulk crystals of size $5\times4\times3$ mm$^3$ were grown by optimized growth parameters with a flux-charge ratio of 6:1. The size of the single crystals by slow cooling technique is restricted due to the large evaporation of flux. Surface morphology of the grown crystals shows step and hopper growth pattern due to changes in supersaturation. Back reflection Laue pattern showed ‘ab’ plane of trigonal lattice and clear diffraction pattern. LPMO
single crystals showed metal insulator transition ($T_{MI}$) around 247 K and this is lower than $T_c$ (252 K). The observed colossal magneto-resistance was 99% and this may be due to alignment of rare earth/divalent ion under external magnetic field. Large value of CMR was observed at the temperature interval of magnetic inhomogeneity of the samples. It was observed that the magneto-transport properties and removal of cluster under an external field is closely correlated with the field induced colossal change of resistivity accompanying a long range ferromagnetic order.