Structural, magnetic and magneto-resistance properties of La$_{0.88}$Ca$_{0.12}$MnO$_3$ single crystals

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La$_{0.88}$Ca$_{0.12}$MnO$_3$ single crystals of high quality have been prepared by using floating zone technique. Their composition and structure are verified using X-ray diffraction and EDAX. The temperature dependence of the resistance along $ab$-plane and $c$-axis has been measured in the temperature range 77 K to room temperature in the magnetic fields up to 8 T. The $R$-$T$ data along $ab$-plane and $c$-axis shows a similar behaviour and it is the characteristics of insulating behaviour having the resistance 0.7 M$\Omega$ at 90 K and 16.1 $\Omega$ at 300 K. The insulating behaviour persists under the magnetic field up to $H = 8$ T. There is no resistance peak or electronic transition over the whole temperature range studied. However, there is a notable change of resistance at about 120 K, seemingly related to paramagnetic insulator to ferromagnetic insulator transition and is confirmed by magnetization measurement transition at a temperature $T_c = 122$ K. The sharp peak around the same temperature in the heat capacity measurement indicates the onset of long range ordering. The magnetoresistance measured at different magnetic fields shows similar kind of behaviour with some marginal change in the magnitude along $ab$-plane and $c$-axis.

Keywords: CMR, La$_{0.88}$Ca$_{0.12}$MnO$_3$ single crystal, Ferromagnetic - paramagnetic transition, Magneto-resistance

1 Introduction

The colossal magnetoresistance (CMR) hole doped manganites$^{1,2}$ is a topic of current research interest. Doped perovskite - type manganites RE$_{1-x}$A$_x$MnO$_3$, with RE = La, Nd or Pr and A = Ba, Sr, Ca, and Pb are promising magnetoresistive materials in which the change of resistivity by applying magnetic field is so large that this effect is described as colossal. They were studied very intensively in the last few years due to the effect of CMR$^{3-6}$. They exhibit ferromagnetic to paramagnetic (FM-PM) as well as metal to insulator (M-I) transition. The perovskite structure of ABO$_3$ with A = La, Pr, Nd and B = Mn, are paramagnetic insulator at all temperatures. When these insulators are doped with divalent ion, resistivity decreases with formation of Mn$^{4+}$, which reduces the Jahn-Teller distortion, induces double exchange interactions and hence plays a crucial role in the electrical transport and magnetic properties of these oxides$^1$. La$_{1-x}$A$_x$MnO$_3$ perovskite systems have been studied extensively for their remarkable CMR properties that have technological applications. The CMR behaviour occurs near the ferromagnetic (FM) transition temperature and this remarkable phenomenon is attributed to the magnetic coupling between Mn$^{3+}$ and Mn$^{4+}$ ions as well as to the strong electron-phonon coupling arising due to Jahn-Teller splitting of Mn 3d levels. It has also been found that the bond angle and bond length of Mn$^{3+}$-O-Mn$^{4+}$ also play crucial role in controlling the CMR properties of these manganites as the geometric quantity and the tolerance factor are modified when suitable ions are substituted for La to fill the 3D network of MnO$_6$ octahedra$^3$. The problem, however, is that samples used for such studies (typically ceramic, thin films or bulk single crystal) represent properties of samples but not the compound as such. It concerns especially magnetic and electrical characteristics because they are extremely sensitive to the defect structure of samples. In the case of ceramic and thin film samples, these properties are determined mostly by grain boundaries and the substrate-thin film interface, respectively. Bulk single crystals are more preferable for the right investigations, but manganite crystals of the nominal composition demonstrate significantly different magnetic and electric characteristics depending on their mosaicity and/or point defect structure. So preparation of high-quality single crystals of manganites is more important.
Among other methods, the floating zone (FZ) method is most suitable for the growth of CMR manganites. In this paper, the structural, magnetic, thermal and magneto-transport properties of \( \text{La}_{0.88}\text{Ca}_{0.12}\text{MnO}_3 \) single crystals have been studied.

2 Experimental Details

The single crystals of \( \text{La}_{0.88}\text{Ca}_{0.12}\text{MnO}_3 \) were prepared by using floating zone technique. X-ray diffraction study indicated that the materials is single phased. X-ray diffraction data confirmed the quality of the crystal. The composition of the crystals was determined by energy dispersive X-ray analysis (EDAX) using INCA Oxford analyzer attached with scanning electron microscope. The electrical resistance and magnetoresistance (MR) of the crystals were measured as a function of temperature by standard four-probe technique in a superconducting magnet with the maximum applied field 8 T along \( \text{ab}\)-plane and \( \text{c}\)-axis in temperature range 77 K to 320 K. The field direction was parallel to the current direction. Magnetization was measured using Quantum Design PPMS-7 in the temperature range 4 to 300 K. The \( \text{ac}\)-susceptibility was measured using susceptometer as a function of temperature at 3.87 Oe magnetic field. The specific heat was measured by the semi-adiabatic heat pulse method. The temperature was varied by using a commercial liquid nitrogen closed cycle cryostat equipped with a temperature controller. All measurements were carried out in the temperature range \( \text{80-300 K} \).

3 Results and discussion

Figure 1 shows typical EDAX data on the above single crystal. The compositions obtained from the EDAX spectra were close to the expected calculated composition.

The variation of resistance with temperature in the presence of various magnetic fields along \( \text{c}\)-axis, for \( \text{La}_{0.88}\text{Ca}_{0.12}\text{MnO}_3 \) single crystal is shown in Fig. 2. It is the characteristic of semiconducting behaviour having about 6.9 M \( \Omega\)cm at 90 K and 31.5 \( \Omega\)cm at 296 K. Due to magnetic fields, resistance decreases in the low temperature region but near the room temperature (from 200 K), there is a no effect of magnetic field. At about 120 K, there is a notable change of resistance, seemingly related to the possible paramagnetic insulator to ferromagnetic insulator transition (Fig. 5).

Figure 3 shows the variation in resistance with temperature in the presence of same magnetic fields along \( \text{ab}\)-plane. It shows the similar behaviour along \( \text{c}\)-axis. Present results are also compared with previous experimental thin film data on \( \text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3 \), which reveal that in single crystal the resistivity is bit higher, as compared to the thin film although the nature of variation remains the same.

Figures 4 and 5 show the magnetoresistance (MR) as function of magnetic field at various temperature regions for both directions, along \( \text{c}\)-axis and \( \text{ab}\)-plane. In both conditions, behaviour of plots were the same, in low temperature region. MR increases with the magnetic field, but at near 300 K region, there is no effect of magnetic field and it means that the resistance is approximately the same for each magnetic field. The maximum MR is found 55% for 8 Tesla at 120 K.

The temperature dependence of specific heat is shown in Fig. 7. It shows a sharp peak around 116 K.
which is close to the transition temperatures obtained from the other measurements. The sharp peak in the heat capacity data indicates the onset of long range ordering. To estimate the entropy change associated with the transition we subtracted the background, which is obtained by fitting the measured heat capacity data excluding peak region with a polynomial. The magnetic heat capacity thus obtained showed an entropy change of 1.2 J/mol K.

4 Conclusions

The structural and magneto-transport properties of single crystal of La$_{0.88}$Ca$_{0.12}$MnO$_3$ are reported. All these measurement are consistent with each other to reveal the electronic and magnetic phase transition. The heat capacity data indicates the onset of long range ordering around 116 K. The entropy change
associated with this transition was found to be 1.2 J/mol K.

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