Research Article

Transport, Magnetic, and Thermal Properties of $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ Single Crystal

Tejas M. Tank,¹ Ashish Bodhaye,² Ya M. Mukovskii,³ and Sankar P. Sanyal¹

¹ Solid State Physics Laboratory, Department of Physics, Barkatullah University, Bhopal 462 026, India

² Department of Physics, St. Vincent Pallotti College of Engineering & Technology, Nagpur 441 108, India

³ Moscow State Steel and Alloys Institute, Moscow 117 936, Russia

Correspondence should be addressed to Tejas M. Tank; tejas.physics2020@gmail.com

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We report the transport, magnetic, and thermal properties of $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal. It was prepared using floating zone technique used under oxygen pressure of 1 bar with a typical growth rate of 1 mm/hr. The resistivity data shows the metal to insulator transition (M-I) occurring at $T_{\text{MI}} = 290$ K along the c -axis and at $T_{\text{MI}} = 280$ K along the ab -plane. It is observed that the T_{MI} is higher along the c -axis as compared to that in the ab -plane, thus indicating that more favorable hopping of electrons is along the c -axis. From bolometric application point of view, the temperature coefficient of resistance (TCR) is found to be $\sim 28\% \text{ K}^{-1}$. The ac -susceptibility measurement shows that this material exhibits ferromagnetic to paramagnetic transition temperature (T_C) 277 K. Sharp peak around this temperature in heat capacity data indicates the onset of long-range ordering. The entropy change associated with this transition is found to be 2.3 J/mol K.

1. Introduction

The colossal magnetoresistance (CMR) of hole doped manganites $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$, with RE = La, Nd, and Pr and A = Ba, Sr, Ca, and Pb, is promising magnetoresistance 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 [1–4]. 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, and Nd and B = Mn, is paramagnetic insulator at all temperatures. When these are doped with divalent ion, their resistivity decreases with formation of Mn^{+4} , which decreases the Jahn-Teller distortion, creates double exchange interactions, and hence plays a crucial role in the electrical transport and magnetic properties of these oxides [1]. $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ perovskite systems have been studied extensively for their remarkable CMR properties that have technological applications [5]. The CMR behavior 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 $\text{Mn}^{+3}-\text{O}^{2-}-\text{Mn}^{+4}$ play a 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 [6]. The problem, however, is that samples used for such studies (typically ceramic, thin films, or 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. The 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 manganite is more important. We have chosen $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal as $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [7] and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [8], which exhibit a Curie transition below and above room temperature, respectively. Therefore it is expected that the solid solution between end members, that is, the compounds with $0 < x < 0.33$, might have the Curie temperature in between (i.e., around room temperature), leading to magnetocaloric and magnetoresistive temperature working range relevant to device designed at ambient condition. Earlier, no such efforts have been made, so the present results could not be compared with earlier work.

Among other methods, the floating zone (FZ) method is most suitable for the growth of CMR manganite. In this paper, the transport, magnetic, and thermal properties of $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal have been studied.

2. Experimental

The single crystal of $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ was prepared by using floating zone technique with radioactive heating under oxygen pressure of 1 bar with a typical growth rate of 1 mm/hour. The size of crystal was 4.76 mm in diameter and 3.2 mm in length. Temperature dependence of electrical resistivity was measured using standard four-probe method along ab -plane and c -axis in temperature range 77 K to 300 K. The ac -susceptibility was measured using susceptometer as a function of temperature at 3.87 Oe magnetic field and an exciting frequency of 131.11 Hz. The specific heat was measured by the semiadiabatic 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 80–300 K [9].

3. Results and Discussion

Typical plot of resistivity versus temperature for $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal along ab -plane and c -axis is shown in Figure 1. Such a study was undertaken so as to estimate the direction dependence of charge flow. It is seen from Figure 1 that along ab -plane there is a large increase in resistivity (of about five times) as compared to that along c -axis. Such an evolution is a characteristic of an insulator to metal (I-M) transition with decreasing temperature coinciding with an abrupt change of the magnetic state. Here the resistivity shows a peak at 280 K, which separates the high temperature paramagnetic insulating phase from the low temperature ferromagnetic metallic phase. It is noted that the M-I transition temperature is higher and its magnitude is less than that of ab -plane. This is expected, as the Mn–O–Mn bond along c -axis is linear (i.e., 180°), while the same along ab -plane is nonlinear. Thus the hopping of electron is favorable along the c -axis and not in the ab -plane. This can be understood from metal to insulator (M-I) transition at $T_{\text{MI}} = 290$ K along c -axis. The magnitude of resistance along the c -axis is small (of the order of 1Ω).

FIGURE 1: Resistivity versus temperature plot for the single crystal of $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$.

FIGURE 2: TCR versus temperature plot for the single crystal of $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$, along ab -plane and along c -axis.

To evaluate the possibility of this single crystal for sensor application point of view, we have calculated the temperature and the field sensitivity of resistivity. This parameter is quantified in terms of temperature coefficient of resistance (TCR) and is shown in Figure 2.

Consider the following:

$$\left[\text{TCR} = \left(\frac{1}{R} \right) * \left(\frac{dR}{dT} \right) * 100\% \right]. \quad (1)$$

It seems that the maximum TCR value we got along c -axis is $28.6\% \text{ K}^{-1}$ whereas along ab -plane value of TCR is $21\% \text{ K}^{-1}$. This is expected, as the Mn–O–Mn bond along c -axis is linear (i.e., 180°). Such large TCR values are a highly desirable goal in the context of the development of highly responsive bolometer.

FIGURE 3: Real part of ac -susceptibility for $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal.

The temperature dependence of the real part of ac -susceptibility has been measured at fixed applied field of 3.87 Oe and an exciting frequency of 131.11 Hz. This result is shown in Figure 3. The $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal undergoes a phase transition from paramagnetic to a ferromagnetic state at the Curie temperature $T_C = 277$ K. Therefore, the magnetic measurement is in good agreement with the resistivity results. Plot shown in the inset is the evidence for short-range ferromagnetic correlations that emerge from the susceptibility measurements. The Curie-Weiss behavior is followed above $1.0 T_C$, but below this temperature the behavior clearly indicates the presence of short-range ferromagnetic correlations which is in good agreement with the resistivity and specific heat results.

The temperature dependence of specific heat of $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal is shown in Figure 4. It shows a deviation from the onset ferromagnetic ordering around 276 K, which is close to the transition temperature obtained from the ac -susceptibility and resistivity measurements. A comparison of these data with that of LCMO single crystal [7] shows that by codoping of Sr, we have achieved a larger transition temperature (near the room temperature) which can be useful for device application. This change 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 entropy change associated with this transition is found to be 2.3 J/mol K.

4. Conclusion

All these measurements are consistent with each other to reveal the electronic and magnetic phase transition in CMR single crystal investigated by doping small amount of Sr (0.06%). This study reveals that the magnetic transition temperature increases substantially to 277 K and also matches

FIGURE 4: Specific heat versus temperature for $\text{La}_{0.7}\text{Ca}_{0.24}\text{Sr}_{0.06}\text{MnO}_3$ single crystal.

with heat capacity data which indicates the onset of long-range ordering around 276 K around room temperature, and large TCR values are a highly desirable goal in the context of the development of highly responsive bolometer device application.

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