Effects of low pressure plasma irradiation on electrical resistivity of perovskite oxide $Eu_{1-x}Sr_xMnO_3$

U. Deka$^1$ and A.Rao$^2$

$^1$Department of Physics, Sikkim Manipal Institute of Technology, Majitar, Rangpo, East Sikkim-737136, India
$^2$Department of Physics, Manipal Institute of Technology, Udupi, Manipal, Karnataka-576104, India

Email: udeka1@rediffmail.com

Abstract. The use of perovskite type compounds, has gained a tremendous applications in various fields like memory storage devices, bolometers, superconductors, solar cells, etc. One of the very important uses of perovskite material is in the construction of bolometers. Bolometers are extensively used in fusion devices for temperature measurement and also in space application. In this paper we have presented the experimental behaviour of the electrical resistivity of the perovskite oxide $Eu_{1-x}Sr_xMnO_3$ after plasma exposure for different composition. It is found that the compound $Eu_{1-x}Sr_xMnO_3$ behaves as an insulator for all the values of $x$, since the effective single electron bandwidth is very narrow. The observed decrease in the resistivity below $T_{MI}$ may be due to the lack of delocalized carriers that contributes for the metallic nature of the sample.

1. Introduction
The discovery of the perovskite mineral chemically represented as $ABO_3$, where $A$ and $B$ are two cation of very different sizes and $O$ is an anion that bonds the both. This has been a boon for the material scientists. There has been an upsurge in the research of the family of the perovskite material because of its multifaceted engineering applications spreading over a wide discipline from energy production (SOFC technology) [1], environmental containment (radioactive waste encapsulation) [2] communications (dielectric resonator materials) [3], bolometers for radiation measurement [4], solar cells [5], high $T_c$ superconductors [6], etc. The challenge for increase in the efficiency of solar cells has led to an upsurge in the material research. The solar cells used in space applications are continuously exposed to the space plasma. The effect of plasma on perovskite material forms an important part of research to understand the efficiency of the solar cells under various plasma conditions.

The use of bolometers for measurement of radiation power loss in fusion devices is very common. The spatially and temporally resolved measurements of total (broad band) radiated power loss (and also losses from neutral particles) from a high temperature plasma can be effectively made by bolometer [7]. Bolometers diagnostics can be used to measure the radiation over a wide spectrum, from the soft x-rays to the infrared, with a nearly uniform response at all wavelengths. The impetus in the study of temperature sensitivity of perovskites materials for construction of bolometer has gained
lot of momentum in recent years [8,9]. But the research about the effect of plasma on such materials is very less and has left a wide scope to delve into this area from experiment to theory.

The challenge for manufacturing of new ceramic materials to withstand radiation damage and bubble nucleation at micro-structural traps in the core of fusion and fission devices is still wide open. In this regard lot of research has been carried out to study the effect of radiation damage on perovskite materials. The requirement of structural stability due to impingement of high energetic particles was of high demand. The physics of phase transformation from crystalline to amorphous under the irradiation of energetic ion beams holds a clue to develop new materials [10]. It was shown that the interaction amongst irradiation induced defects plays a major role for the phase transformation. The defects density depends upon the temperature and the recovery of the defects are responsible for the kinetics of amorphization. Similar studies were carried out by different authors to understand the effect of high energy electron beam [11,12]. They have shown that energy of the electron beam is a determinant factor in the variation of the bond angle and bond length. Such distortion vastly controls different physical properties like electrical resistivity, colossal magnetoresistance, thermal conductivity, etc. These effects have been explained with the help of different theoretical models proposed by different workers as mentioned in the paper.

Since plasma is a collection of both electrons and ions, so the simultaneous effect of both the species might reveal some new properties of perovskite materials. In one such work by Kim et al. [13], they have investigated the effect of oxygen plasma on the behaviour of colossal magnetoresistivity of manganite perovskite, $La_{0.7}Ca_{0.3}MnO_3$. In their study, they showed that oxygen plasma exposure can also induce structural defects. Such kinds of defects are responsible for the variation of different electrical and magnetic properties like broadening of the resistive transition, the metal–insulator transition temperature, etc. Henceforth, this become pertinent that the plasma irradiation can induce modification in the physical properties of perovskite materials, which may not necessarily be same as in case of ion beam or electron beam irradiation.

In this work we have carried out a particular experiment to study the effect of low pressure air plasma on the electrical resistivity of $Eu_{1-x}Sr_xMnO_3$. The major focus of this work has been to observe the variation of the electrical resistivity for different concentration of doping for a given plasma exposure time.

2. Experimental details

We have prepared the $Eu_{1-x}Sr_xMnO_3$ for four different doping concentrations with values of $x = 0.2$, 0.3, 0.4, 0.5. The standard solid state reaction method was used to produce the perovskite materials. The detail procedure of material preparation, experimentation and testing are discussed below.

2.1 Preparation of the series $Eu_{1-x}Sr_xMnO_3$

We take the parent composition as $EuMnO_3$. We consider the stoichiometric ratios of high purity materials of $Eu_2O_3$(99.99%) $SrCO_3$ and $Mn_2O_3$(99.9%) from Sigma Aldrich(99.99%) which are mixed together and ground for 5 hours in a mortar and pestle. Then the mixture is calcined at 1000°C for 24 hrs. After that it is again ground for 1 hour and then calcined again for 24 hours at 1200°C. It is then sintered at 1350°C for 36 hours. Then pellets were made under pressure of 100 N/m².

2.2 Plasma Irradiation

The plasma set up comprises of a cylindrical vessel of 37 cm long and 21 cm diameter evacuated by a rotary and diffusion pump. Plasma is produced by creating electric discharge of the air between two circular stainless electrode of thickness of about 0.36 mm and diameter of 6cm. The electrodes are kept at 11cm apart. A variable dc power supply up to 1 KV is used to produce plasma with a grounded anode.

The discharge chamber was properly cleaned with acetone and after drying it glow discharge air plasma air was produced at a pressure of $10^3$ mbar. Initially the chamber was cleaned of the dust particles due to plasma bombardment of the surfaces. After the cleaning, $Eu_{1-x}Sr_xMnO_3$ pellets with
four different concentration of doping were kept using sample holders between the two plates with the samples facing the electrodes so that the samples are exposed to maximum plasma bombardment. Even though air was used for the discharge, the chamber was evacuated to a pressure of $10^{-3}$ mbar and then air was inserted from a cylinder to bring the working pressure to 0.2 mbar. After that dc voltage of $660 \pm 1$ V is applied between the two electrodes to discharge the air. A constant plasma current of $110 \pm 0.5$ mA was maintained to achieve moderately high power plasma. The discharge voltage applied for the given electrode separation of 6 cm at 0.2 mbar was sufficient to ionize the Oxygen, Nitrogen and Argon in air [14-16]. Hence, multicomponent and collisional plasma was produced showing a distinct glow. Since our samples are rectangular bars, we chosen the plasma power to be higher than that required for electrical properties modification of metallic thin film [13, 17] due to air plasma. The measured plasma power was 102.85 W. The samples were treated with plasma for exposure of 60 s. The pristine and the plasma treated samples are than tested for their electrical properties.

2.3 Resistivity Measurement

Resistivity measurement is easy and straight forward method, which provides information about the electrical properties of the sample. The measurement of electrical resistance as a function of temperature gives information about the various temperature dependent electronic phase transitions. The resistivity is measured using conventional four-probe method in a closed cycle refrigerator (CCR) (Model No. JANIS-CCS100/202) in the temperature range of 10 K- 400 K. To measure resistivity using this technique, the samples were typically cut into rectangular bar shapes of dimensions 12 mm × 6 mm × 1.5 mm with ± 0.1 mm in all the dimensions using a rectangular die set and hydraulic press. For the electrical contacts of the probes silver paint was used. This silver paste was applied at the ends for current and voltage contacts. Due to very less resistance, thin copper wires were connected with silver paint and the whole assembly was put onto a sample holder, where the wires were connected with leads to the measuring instruments. All the four contacts were connected to the measurement system where two end leads were used to pass stable DC current using a precise current source (Model 6221), which can pass current of a few microamperes and the other two were connected to high precise nano-voltmeter (Model 2182A) to measure the voltage across the samples. The resistance was estimated using the well-known Ohm’s law using equation $R=V/I$. The dc resistivity was calculated using the expression, $\rho = RA/L$ where $A$ is the area of cross section of the sample and $L$ is the distance between the voltage probes, which was 1mm for our setup.

3. Results and discussion

The experimental observation about the electrical resistivity has shown very interesting results before and after plasma irradiation. The observed results are very much different from electrical resistivity measurement due to electron beam irradiation. Even though the penetration depth was not measured but for the considered plasma parameters, the modification will occur only near the surface. It is observed that the typical penetration depth in plasma immersed ion implantation with pulse duration of ~10μs with high biasing voltage ~10 KV is ~10 nm [18]. Comparing our plasma parameters, the penetration depth will be very small and of the order of few nanometres.

| $x$ ($Sr$) | $T_{MI}$ (K) | $\rho(T_{MI})$ kΩ-mm | $T_{MI}$ (K) | $\rho(T_{MI})$ kΩ-mm |
|-----------|-------------|----------------------|-------------|----------------------|
| 0.2       | 92.591      | 951.82368            | 79.461      | 1433.07577           |
| 0.3       | 14.04       | 108.6418             | 49.689      | 1256.45704           |
| 0.4       | 12.849      | 7.05741              | 63.937      | 52.08283             |
| 0.5       | 12.997      | 861.57195            | 12.91       | 183.22877            |
Since electrical conduction is mainly a surface phenomenon, hence the surface modification of the sample has exhibited distinct variation in the electrical properties. It is found that there is substantial modification of the electrical resistivity of the perovskite material after the plasma irradiation. The electrical resistivity of both unexposed and exposed samples were measured at different temperature and for different strengths of doping mentioned by ‘x’ (0.2, 0.3, 0.4, 0.5) on the A side of the compound perovskite. The electrical resistivity, $\rho(T)$ for the pristine and plasma irradiated samples namely $Eu_{1-x}Sr_xMnO_3$ were measured by varying the temperature from 10 to 300 K. The error in the measurement of resistivity is less than 1%. We observe that the metal to insulator transition temperature, $T_{MI}$ varies along with the resistivity for different samples and also after plasma irradiation. The detailed discussions are given below.

![Figure 1. Variation of resistance with temperature before and after the plasma exposure for $Eu_{1-x}Sr_xMnO_3$](image-url)

In fig. 1 the combined plot of electrical resistivity, $\rho(T)$ of the pristine and plasma irradiated samples for $Eu_{1-x}Sr_xMnO_3$ is shown. Even though we couldn’t observe transitions from metal to insulator but the maximum on the lower temperature side may be assumed as the beginning of the
semiconducting and insulating behaviour. We can see that the peak temperatures are different for all the four different concentrations of Eu. It is quite evident that the $T_{MI}$ varies with amount of doping. Moreover, it is clearly noticeable that the electrical resistivity at $T_{MI}$ varies appreciably and the value of $T_{MI}$ also varies in most of the cases. Interestingly, we see that the amount of variations with the level of doping is not uniform. The variations in electrical resistivity and $T_{MI}$ for all the cases are given in Table 1.

The electrical resistivity also undergoes transition from low temperature metallic to high temperature insulating state. When the electrical resistivity of the pristine sample of Europium (Eu) for doping concentration of $x=0.2$, $0.3$, $0.4$ and $0.5$ was measured by cooling the sample from room temperature to a very low temperature around 10 K, we observe that the resistivity increases as shown in figure 1. The resistivity increases with decreasing temperature after plasma irradiation.

We didn’t observe any metal to insulator transition in the temperature range of 10 K -300 K indicating the presence of only semiconducting state under ambient pressure. Similar results were observed for $x=0.42$ for $Eu_{1-x}Sr_xMnO_3$ under ambient pressure by Kosaka, et. al. [19] also for unirradiated sample. However, when the samples were exposed to air plasma for 1 min as mentioned before, the electrical resistivity increases sharply for $x=0.2$, $0.3$ and $0.4$ and the $T_{MI}$ also varies. But for $x=0.5$, we didn’t observe a similar behaviour as compared to the other doping concentrations. For this particular case the resistivity rather decreased sharply and $T_{MI}$ remained unaffected. The $T_{MI}$ for the different values of $x$ is given in Table 1 and the corresponding plots are given in Fig 2 and 3. The time of exposure plausibly may not affect the $T_{MI}$, since plasma beam irradiation may induce interstitial defects, which are quantum mechanical phenomena. Of course, a detailed investigation with different time of exposure and different plasma power will give was more insight into the physics about the observations.

![Figure 2. Variation of metal-insulator transition temperature before and after the plasma exposure for $Eu_{1-x}Sr_xMnO_3$.](image)
The variation of $\log(\rho)$ w.r.t $1/T$ for $x=0.2$ for $Eu$ is shown in figure 4. It is seen that the curve of $\log(\rho)$ w.r.t $1/T$ is mostly linear in the higher temperature region but get curved with $d^2\rho/dT^2>0$ for higher values of $x$ in lower temperature region in most of the cases. The nature of the curve remains same for the plasma irradiated samples also. Thus we can say $dp/dT<0$, i.e. temperature dependence is more like semiconductor for most of the values of $x$ for all the dopants. The electronic conductivity increases with increasing doping concentration because of which the value of electrical resistivity, $\rho$ decreases [20-23]. The composition dependence of $\rho$ on $x$ corresponds to the evolution of $Mn^{4+}$ states among the majority of $Mn^{3+}$ states.
We would like to put forward some other plausible reasons for the variation of electrical resistivity of the different perovskite samples after plasma irradiations. The compound \( \text{Eu}_{1-x}\text{Sr}_x\text{MnO}_3 \) behaves as a semiconductor for all the values of \( x \) and the resistivity increases after plasma irradiation except for \( x=0.5 \). The variation after irradiation may be because of disorder induced near the grain boundaries as reported in case of different perovskites [23]. Our experimental results for \( \text{Eu}_{1-x}\text{Sr}_x\text{MnO}_3 \) also verify the same. This behaviour indicates that the carriers are more localised around the hump reason thus prevents the transition at that temperature. Such behaviour implies that the localization of charge carriers near the hump like region is strong. The observed decrease in the resistivity below \( T_{MI} \) may be due to the lack of delocalized carriers that contributes for the metallic nature of the sample.

Another reason for such change is also may be increase in \( \text{Mn-O-Mn} \) bond angles which leads to the increase in the probability of charge carriers hoping between adjacent \( \text{Mn}^{3+} \) and \( \text{Mn}^{4+} \) sites, which reduces the resistivity as reported by the authors when irradiated with electron beam [23].

4. Conclusions

The electrical properties of a perovskite material both unexposed and exposed to plasma were measured. It was found that the electrical properties of the perovskite material get affected by plasma irradiation. There was significant variation in resistivity for different level of concentration of the dopant, \( x \). This kind of behaviour can be seen in semiconductors where the resistance increases with decreasing temperature. The unusual behaviour of temperature-resistance relationship of perovskite material may be due to plasma effects. There is every possibility that after plasma irradiation structural changes like change in bond length, bond angle, etc must have occurred as normally observed in cases of electron beam or ion beam irradiations. More characterisation like XRD, SEM will be required to understand the underlying physics of the variation of the physical characteristics and will be carried out. From the above results and discussions we conclude that the electrical resistivity of a perovskite material can be modified by the plasma. They can be more modified if the time of exposure is also increased.

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