Influence of electron beam irradiation on electrical, structural, magnetic and thermal properties of Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ manganites

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1. Introduction

Manganese oxides with perovskite structure provide a gateway to study the interplay of various properties such as structural, electrical, and magnetic phases of matter in a strongly correlated system. The perovskite manganites with general formula $RE_xAE_yMnO_3$ (where $RE$ and $AE$ are rare-earth and alkaline-earth ions, respectively) have been extensively investigated for more than two decades due to a wide variety of physical properties exhibited in these materials such as superconductivity, colossal magnetoresistance (CMR), ion conduction, magnetism and dielectric behavior [1–4]. Generally manganites are known to show strong electron correlation. In such systems, spin, charge, orbital, and lattice degrees of freedom are strongly coupled, thereby resulting in various ground states such as ferromagnetic and charge/orbital ordering states. These ground states have comparable energies so that an external disturbance can easily drive the system from one state to another. This leads to the coexistence of phases with different magnetic and electronic properties. The understanding of the fundamental origin of these ordered phases and their dynamic interplay are still an important scientific challenge. The basic physical principle of manganites is mainly due to the competition between the delocalization effects of the electronic kinetic energy and the localization effects of the Coulombic force of repulsion. When the kinetic energy is dominant, one finds a metallic ground state with ferromagnetic alignment. On the other hand, when the localization effects are dominant, insulating behavior with anti-ferromagnetic ground state is observed. There are few models that can explain the transport mechanism in manganite systems. However, most of them can be only applied to either the ferromagnetic (FM) or the anti-ferromagnetic (AFM) region. In the semiconducting region, the transport mechanism can be explained by Mott’s variable range hopping (VRH) model, small polaron hopping (SPH) model, and the adiabatic small polaron...
hopping (ASPH) model [5]. In the metallic region, the transport mechanism is generally governed by the scattering mechanisms such as single magnon, electron-magnon, electron-electron and electron-phonon processes [6,7]. Recently a theoretical percolation model based on phase segregation between metallic and semiconductor regimes has been proposed [8,9]. It is established that such a model could satisfactorily describe various transport properties of manganites in the entire temperature range. Further, the Kondo like upturn observed in resistivity at low temperatures can be addressed using modified percolation model proposed by Dhahri et al. [10]. The theoretical percolation model has also been used to explain the behavior of Seebeck coefficient as a function of temperature [11–14]. However, in the case of Seebeck coefficient, the observed upturn (Kondo like) behavior has not been properly explained using percolation model. Hence, a theoretical attempt on this issue is in order.

Among the rare earth based compounds, praseodymium (Pr)-based CMR materials are of great interest. The parent compound Pr0.8Sr0.2MnO3 exhibits only anti-ferromagnetic insulator behavior whereas Pr1−xAEx/Sr, MnO3 compounds show different resistivity trends [6,8] and phase separation (PS) [6,14–18]. Pr-based manganites are potential candidates for various applications such as resistance random access memories (RRAM) in the next generation of non-volatile memories which has led to dramatic improvements in the data density and reading speed of magnetic recording systems. This is mainly attributed to the bipolar resistive switching (RS) behavior observed in these compounds [19–21]. Various physical characteristics such as electronic, and magnetic properties can be tailored by applying external perturbations like magnetic field, pressure and irradiation [22–29]. The most common method used to crystallize any system is by thermal annealing, but the size of the grains increases during this process and it is perhaps difficult to have control over the grain size of the crystal. Irradiation with energetic particles such as electrons, ions, and neutrons has been one of the better and efficient methods to achieve structural control as a good alternative to thermal annealing [27–29]. Radiation-induced disorder in manganites has been investigated and it is demonstrated that irradiations with electron beam/i on beam change the Mn–O bond lengths and Mn–O–Mn bond angles which can shift the magnetic phase transition temperatures [22–26].

To the best of our knowledge, no studies have been done on the effect of electron beam irradiation on electrical, magnetic and thermal properties of Pr1−xSr,MnO3 compounds. It is well known that Pr1−xSr,MnO3 compounds show different resistivity trends which depends on the value of x. Samples with 0 ≤ x ≤ 0.15 are canted anti-ferromagnetic, while a ferromagnetic to anti-ferromagnetic transition is observed for samples with x ≥ 0.2. Hence Pr0.8Sr0.2MnO3 compound is of great interest and there are some reports on magnetic and electrical studies on such a system in the literature [3,30–34]. However, there is no study on thermal properties such as thermal conductivity, Seebeck coefficient, and specific heat for Pr0.8Sr0.2MnO3. In this work, we report a detailed study regarding the effect of electron beam irradiation on the structural, electrical, magnetic and thermal properties of Pr0.8Sr0.2MnO3 samples. In particular, we demonstrated that the theoretical percolation model can successfully explain the electrical and thermoelectric transport mechanism in the entire temperature range for the Pr0.8Sr0.2MnO3 system.

2. Experimental details

Polycrystalline samples of Pr0.8Sr0.2MnO3 were synthesized using conventional solid state reaction method. For preparation, stoichiometric mixture of Pr2O3, SrCO3 and MnO2 powders (99.9% Sigma-Aldrich) was ground and the fine powder was calcined thrice at 1000 °C for 24 h with intermediate grindings. From the same batch of powder, pellets were made with application of identical pressure using a hydraulic press. Then the pellets were sintered at 1300 °C for 36 h and were cooled naturally inside the furnace to room temperature. The electron beam irradiation was carried out in a 10 MeV linac (Linear particle accelerator). The accelerator was operated at beam energy of 7.5 MeV with beam power of 1.5 kW and beam parameters were optimized to deliver uniform surface dose. The irradiation was performed at room temperature for 50 kGy, 100 kGy and 200 kGy. XRD was carried out to analyze the crystal structure and microstructure of crystalline solids using Mini Flex II DESK TOP X-ray Diffactometer which uses Cu-Kα as the source (wavelength, λ = 1.541 Å). The electrical resistivity of the samples was measured using a conventional four probe technique. The resistivity measurements were carried out in a closed cycle refrigerator as a function of temperature in the range 10–300 K. The magnetic measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer and 9 T PPMS based vibrating sample magnetometer (VSM) (both Quantum Design) in both zero-field-cooled (ZFC) and field-cooled (FC) conditions at external magnetic field of 250 Oe. The hysteresis loops (M versus H) of the samples were also recorded at typical temperatures of 5 K and 300 K. Thermal conductivity and Seebeck coefficient measurements were carried out simultaneously in the temperature range 10–300 K using a direct pulse technique. Both the measurements were performed on a warming cycle. For the thermal conductivity measurements, samples were shaped to rectangular bars of dimensions of about 1.5 × 1.5 × 5.0 (mm3). One end of the sample was attached on a copper block, which functioned as a heat sink. A small calibrated chip resistor was fixed at the other end of the sample which acted like a heat source. The temperature gradient was measured using an E-type differential thermocouple fixed directly on the sample which was electrically insulated from the sample. In order to minimize the heat radiation, the temperature difference was controlled to less than 1 K. The Seebeck voltage was detected using a pair of thin Cu wires electrically connected to the sample with silver paste at the same position as the junctions of thermocouple. The elimination of stray thermal emf was achieved by applying long current pulses to a chip resistor that also serves as a heater where the pulses appear as an off-on-off sequence. Specific heat measurements were performed in the temperature range 80–350 K using an ac calorimeter. The details of these thermal measurements are given elsewhere [6,7].

3. Results and discussion

3.1. X-ray diffraction studies

The X-ray diffraction data were recorded at room temperature for the pristine and as well as electron beam irradiated samples. It is revealed from Rietveld refinement analysis that all the samples were crystalline and single phased (within experimental limits of XRD) with an orthorhombic distorted structure (Pbnm). Fig. 1 shows the results of Rietveld refinement of the XRD patterns recorded for pristine and irradiated samples. The calculated pattern is in excellent agreement with the experimental data and the final refinements are satisfactory, in which R-factor and χ2 (goodness of the fit) are fairly small. Lattice parameters were calculated from the refinement.

As shown in Fig. 2(a), it has been noticed that with increasing dosage of electron beam irradiation, a decrease in cell parameters (a or b or c) is observed for the lower dosage 50 kGy sample while
they gradually increase for the 100 kGy and 200 kGy samples. Usually irradiation with energetic particles causes two most prominent effects to crystalline solids viz. i) creation of vacancy or point defects of displacement type and ii) excitation related processes involving relaxation of the bond due to strain or rearrangement of unstable bonds [27–29]. The initial decrease in the cell parameters is presumably due to the production of point defects for the lower dosage of 50 kGy sample. For the higher dosage samples, the relaxation of the strain dominates over the effects created by point defects in the Pr0.8Sr0.2MnO3 system. A similar behavior is seen in the case of bond length where the Mn–O bond length which first decreases for the 50 kGy sample, then an increase in bond length is observed for samples with higher dosage of electron beam (Fig. 2(b), red curve). The reason for this trend is the same as explained in the case of lattice parameters. However, we observe that the Mn–O–Mn bond angle of the studied samples increases monotonically with increase in the dosage of electron beam (Fig. 2(b), black curve). The increase in bond angle is possibly because of the strains induced by the EB irradiation [35].

The EB irradiation not only modifies the Mn-O distance and the Mn-O-Mn angle, but also could cause a distortion in the system [28,35,36]. Generally irradiation induces local distortions of the Mn-O-Mn angle in the crystal structure and consequently causes a random distribution of the magnetic exchange interactions [29]. The relaxation due to the induced strain caused by EB irradiation may result in a larger rotation of the MnO6 octahedral. It is clearly evident from the analysis of the presently investigated samples that the relation $\frac{c}{a} < a < b$ is valid for all the samples, which is a typical characteristic of an orthorhombic system and it is formed by the strong cooperative Jahn-Teller deformation which induces the charge ordering and octahedral distortion [37]. The percentage of orthorhombic deformation $D\%$ can be obtained using the formula [37,38],

$$
D\% = \frac{1}{3} \sum_{n=1}^{3} \left| \frac{d_n - \bar{a}}{\bar{a}} \right| \times 100
$$

where $a_1 = a; a_2 = b; a_3 = \frac{c}{a}; \bar{a} = \left( \frac{a+b+c}{3} \right)^{\frac{1}{2}}$. The $D\%$ value for the pristine sample estimated by using Eq. (1) is found to be 0.11%, and drop to about 0.09% for the irradiated sample with dosage of 50 kGy. With further increase in EB dosage, a gradual increase in $D\%$ is noticed (Fig. 2(c), black curve). As mentioned earlier, this parameter is a measure of the MnO6 octahedral distortion and also is a direct consequence of the octahedral tilting. The magnitude of the octahedron tilt $\varphi$, $\varphi = \tan^{-1} \left( -\sqrt{48} \times z(001) \right)$ is measured considering the positional parameter $z(001)$ which is obtained using Rietveld refinement [37]. It may be mentioned that the stacking of the short range Mn-O bonds along the z-direction is mainly responsible for the orthorhombic distortion [39]. The calculated values of $\varphi$ and $z(001)$ both follow the same trend as $D\%$ which justifies that they are directly related to $D\%$. The observed change in $D\%$ clearly indicates the presence of slight distortion in the system due to irradiation and the magnitude of distortion is higher in the sample with high dosage of irradiation.

In order to verify the correlation between the structural properties with electrical properties, one-electron bandwidth ($W$) is estimated, where $W$ is a measure of delocalization of electrons [35,40,41]. One-electron bandwidth is an important parameter in the ABO3 oxide materials for the existence of the charge order orbital tendency. The relative $W$-value is expressed as,
conclude that the induced insulator to metal transition of Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ decreases gradually. This implies that the energy of double exchange is weakened as the irradiation dosage is increased [35]. We observe that for sample of 50 kGy electron beam dosage, $W$ decreases slightly. With further increase in EB dosage, $W$ increases. As mentioned earlier, EB irradiation increases the Mn–O–Mn bond angles that leads to an increase in the probability of charge carrier hopping between adjacent Mn$^{3+}$ and Mn$^{4+}$ sites, which in turn decreases the resistivity [42]. For the 200 kGy irradiated sample, the enhancement in the resistivity can be attributed to the deterioration of the octahedral structure and may as well be due to the increased strain that introduces magnetic disorder and non-magnetic phase fraction to the sample, resulting in the observed increase in resistivity. An upturn is observed in the resistivity curve of the pristine sample and gets gradually suppressed with irradiation. The origin of the upturn in resistivity can be associated with the competition between the weak localization effect, electron-electron scattering and electron-phonon scattering processes [10]. To understand the nature of the resistivity behavior, various theoretical models can be used. We now explain the low temperature (metallic region) and the high temperature resistivity (insulating region) behavior.

3.2. Electrical resistivity

The electrical resistivity as a function of temperature $\rho(T)$ is shown in Fig. 3. It is clearly seen from the electrical resistivity data that all the samples undergo transition from the low-$T$ metallic state to high-$T$ insulating state. As the temperature decreases from room temperature, there is an evident hump for all the samples before the metal to insulator transition temperature ($T_{\text{MI}}$), and beyond this $\rho(T)$ curve increases till it reaches the transition temperature; thereafter a metallic behavior is observed. This indicates that the carriers are more localized around the hump region thus preventing the transition at that temperature. It is seen that all samples exhibit a similar $T$-dependent resistivity, even for the sample with a high dosage of EB irradiation. Such a finding implies that the localization of the charge carrier near the hump-like region is robust. The observed reduction in the resistivity below $T_{\text{MI}}$ can be attributed to the lack of delocalized carriers that contributes for the metallic nature in the sample. We now explain the effect of irradiation on $\rho(T)$. From Fig. 3, it is evident that resistivity decreases with increase in EB dosage up to 100 kGy. With further increase in EB dosage, resistivity increases. As mentioned earlier, EB irradiation increases the Mn–O–Mn bond angles that leads to an increase in the probability of charge carrier hopping between adjacent Mn$^{3+}$ and Mn$^{4+}$ sites, which in turn decreases the resistivity [42]. For the 200 kGy irradiated sample, the enhancement in the resistivity can be attributed to the deterioration of the octahedral structure and may as well be due to the increased strain that introduces magnetic disorder and non-magnetic phase fraction to the sample, resulting in the observed increase in resistivity. An upturn is observed in the $\rho(T)$ at low temperature ($\sim 31$ K) for the pristine sample and gets gradually suppressed with irradiation. The origin of the upturn in resistivity can be associated with the competition between the weak localization effect, electron-electron scattering and electron-phonon scattering processes [10]. To understand the nature of the resistivity behavior, various theoretical models can be used. We now explain the low temperature (metallic region) and the high temperature resistivity (insulating region) behavior.

\[ W \propto \frac{\cos \left( \frac{1}{2} (\pi - \gamma) \right)}{d^5} \]

where $\gamma$ is the Mn–O–Mn bond angle and $d$ is the Mn–O bond length. It is observed that for sample of 50 kGy electron beam dosage, $W$ increases slightly. With further increase in EB dosage, $W$ decreases gradually. This implies that the energy of double exchange is weakened as the irradiation dosage is increased [35]. We conclude that the induced insulator to metal transition of Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ is driven not only by the Pr doping, but also by the diminishing $W$ due to the widened Mn–O–Mn bond angle and the released MnO$_6$ distortion which is a direct consequence of EB irradiation.
In case of manganites, general equation used to fit the electrical resistivity data \( \rho(T) \) can be given by the well known relation \[6,7\]
\[
\rho(T) = \rho_0 + \rho_1 T^{1/2} - \rho_2 \ln T + \rho_5 T^2 + \rho_4 T^{4.5}
\]
where the first term \( \rho_0 \) is the residual resistivity due to grain boundaries. As the polycrystalline sample contains numerous grains, grain boundaries contribute significantly to the resistivity. The second term \( \rho_1 T^{1/2} \) represents the contribution of electron-electron scattering process and is generally dominant up to 100 K \[37,43–45\]. The last term \( \rho_4 T^{4.5} \) arises due to the combination of electron-electron, electron-magnon and electron-phonon scattering processes \[7,45–47\]. For the presently investigated samples, the low temperature electrical resistivity data below the \( T_{GM} \) was fitted using Eq. (3) and the fitting results are shown in the inset of Fig. 3 (red solid lines). We found that Eq. (3) is insufficient to explain the conduction mechanism in the entire low temperature region. In particular the upturn cannot be explained using the model.

In order to explain the origin of the low-\( T \) resistivity upturn, the analysis of the data was done using a model which considers electron-electron interaction, electron-phonon interaction, and Kondo-like scattering. The Kondo effect is usually seen in magnetic electron-electron interaction, electron-phonon interaction, and Kondo-like scattering. The Kondo effect is usually seen in magnetic electron-electron, electron-phonon interaction, and Kondo-like scattering processes \[7,45–47\]. For the presently investigated samples, the low temperature electrical resistivity behavior in the high temperature region, we have used the adiabatic small polaron hopping model \[37,43,48\] which is given by the expression,
\[
\rho(T) = \rho_0 T \exp \left( \frac{E_A}{k_B T} \right)
\]
where \( E_A \) is the activation energy, \( k_B \) is the Boltzmann constant, and \( \rho_0 = \frac{2k_B e^2 \hbar^2}{m^* c^2} \) is the residual resistivity. Here \( e \) is the electronic charge, \( n \) is the density of charge carriers, \( a \) is the site to site hopping distance, and \( \nu \) is the longitudinal optical phonon frequency. For this model to be valid, a plot of \( \ln(\rho/T) \) versus \( 1/T \) should be a straight line. Inset of the Fig. 4 demonstrates that the SPH model can satisfactorily describe the characteristics of \( \rho(T) \) at high temperatures for the \( \text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 \) system. From the theoretical fits, the activation energy values were evaluated and are listed in Table 1. It is found that the activation energy increases with increasing \( EB \) irradiation dosage up to 100 kGy, whereas \( E_A \) decreases with further increase in \( EB \) dosage. It should be mentioned here that Eqs. (4) and (5) could not explain the electrical resistivity behavior near the \( T_{GM} \) region. In order to understand the transport mechanism in the entire temperature range, Li et al. \[8\] have proposed a phenomenological model called percolation model which is based on the phase segregation mechanism. The percolation approach assumes that the materials are composed of both paramagnetic insulating and ferromagnetic metallic regions, whereas the semiconductor-like transport properties are exhibited in the paramagnetic region \[10,44,49\]. Under these considerations, the resistivity for the entire temperature range can be formulated as,
\[
\rho(T) = \rho_{PM}(T)f + \rho_{FM}(T)(1 - f)
\]
where \( f \) is the volume fraction of ferromagnetic domains, and \( (1 - f) \) is the volume fraction of paramagnetic domains. The volume fractions of paramagnetic and ferromagnetic domains satisfy the Boltzmann distribution
\[
f = \frac{1}{1 + \exp\left( \frac{\Delta U}{k_B T} \right)}
\]
where \( \Delta U \) is the energy difference between paramagnetic and ferromagnetic states in this percolation approach. To explain the mechanism involved in the electrical resistivity of the entire temperature range can be rewritten as,

![Fig. 4. Low temperature fitting of resistivity versus temperature. Inset shows the best fit in the high temperature regime.](image-url)
The parameters obtained using percolation fitting of resistivity data are shown in Table 2. It is apparent that a good agreement between the experimental data and theoretical 

trical resistivity behavior in the entire temperature range. The 

conclude that the percolation model is valid to explain the elec-

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pristine</th>
<th>50 kGy</th>
<th>100 kGy</th>
<th>200 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_0$ (Ω mm)</td>
<td>217.103</td>
<td>81.747</td>
<td>112.411</td>
<td>135.442</td>
</tr>
<tr>
<td>$\rho_1$ (Ω mm/K$^{1.5}$)</td>
<td>87.471</td>
<td>3.687</td>
<td>37.603</td>
<td>63.784</td>
</tr>
<tr>
<td>$\rho_2$ (Ω mm/K$^2$)</td>
<td>151816</td>
<td>2.133</td>
<td>41.619</td>
<td>82.25</td>
</tr>
<tr>
<td>$\rho_3$ (Ω mm/K$^3$)</td>
<td>$-3.1 \times 10^{-8}$</td>
<td>$-1.3 \times 10^{-8}$</td>
<td>$-4.8 \times 10^{-8}$</td>
<td>$-4.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\rho_4$ (Ω mm/K$^4$)</td>
<td>0.085</td>
<td>0.0971</td>
<td>0.074</td>
<td>0.072</td>
</tr>
<tr>
<td>$\rho_5$ (Ω mm/K$^5$)</td>
<td>6.1 $\times 10^{-7}$</td>
<td>1.4 $\times 10^{-7}$</td>
<td>3.1 $\times 10^{-7}$</td>
<td>6.1 $\times 10^{-7}$</td>
</tr>
<tr>
<td>$U_{E}$ (K/kB)</td>
<td>5.4 $\times 10^{-20}$</td>
<td>4.1 $\times 10^{-20}$</td>
<td>4.6 $\times 10^{-20}$</td>
<td>5.8 $\times 10^{-20}$</td>
</tr>
<tr>
<td>$T_C$ (K)</td>
<td>172.7</td>
<td>140.7</td>
<td>142.1</td>
<td>160.5</td>
</tr>
<tr>
<td>$R^2$ %</td>
<td>99.8</td>
<td>99.6</td>
<td>99.8</td>
<td>99.8</td>
</tr>
</tbody>
</table>

$$
\rho(T) = \left( \rho_0 + \rho_1 T^{1/2} - \rho_3 \ln T + \rho_4 T^3 + \rho_5 T^4 + \rho_6 T^5 \right) f + \rho_7 e^{\left( \frac{E_A}{k_B T} \right)} (1 - f) 
$$

For the presently investigated Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ samples, we have fitted the experimental data of electrical resistivity to Eq. (8) and the results are shown in Fig. 5. It is apparent that a good agreement between the experimental data and theoretical fit. We thus conclude that the percolation model is valid to explain the electrical resistivity behavior in the entire temperature range. The fitting parameters are tabulated in Table 2.

3.3. Magnetic measurements

The temperature dependent magnetization measurements under zero-field-cooled (ZFC) and field-cooled (FC) conditions are shown in Fig. 6. All the samples show a pronounced magnetic transition from paramagnetic (PM) state to ferromagnetic (FM) state as the temperature decreases from room temperature. With further decrease in temperature, the ZFC magnetization ($M_{ZFC}$) curve diverges from its respective FC magnetization ($M_{FC}$) curve. The temperature at which the abrupt change in the magnetization curve can be considered as the Curie temperature $T_C$ which is attributed mainly to the magnetic ordering of the Mn sublattice [50]. The Curie temperature ($T_C$) of all the samples was calculated from the temperature derivative of the magnetization ($dM/dT$) versus temperature curve and the $T_C$ values are summarized in Table 3. We noticed that the irradiation does not have much effect on $T_C$. It can be clearly seen from the ZFC curve that there is a change in the slope of $M_{ZFC}$ and this step like interruption is observed at a characteristic temperature denoted by $T_{ST}$ which decreases monotonically with dosage of irradiation. Generally, the change in the slope of $M_{ZFC}$ or $M_{FC}$ observed at low temperature region occurs putatively due to the ordering of Pr moments. Such ordering of Pr moments has been found to be the characteristic feature of low doped Pr$_{1-x}$Sr$_x$MnO$_3$ and Pr$_{1-x}$Ca$_x$MnO$_3$ systems [14,16,50].

It is also seen from Fig. 6 that, at low temperatures $M_{FC}$ values for pristine, 50 kGy and 100 kGy samples are higher than those of $M_{ZFC}$, a feature commonly observed in all manganites [6,9,51]. However for the sample irradiated with 200 kGy, $M_{FC}$ values are smaller than those of $M_{ZFC}$ up to a temperature of about 60 K. With further decrease in temperature $M_{FC}$ and $M_{ZFC}$ curves crossover and the value of $M_{FC}$ is again higher than that of $M_{ZFC}$ below 60 K. Such an unusual phenomenon is presumably due to the high dosage of EB irradiation that facilitates the magnetic domains to overcome the pinning in the 200 kGy sample. However, this feature is suppressed when the temperature is further decreased due
To understand the strength of the magnetic coupling in the present system of Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ samples, the magnetization data below $T_C$ were fitted using the following equation [51]

$$M(T) = M(0) - bT^{3/2} - cT^{5/2}$$

(9)

where $M(0)$ is the magnetization at 0 K and $b$ and $c$ are constants, and $D$ is the stiffness constant. A typical $M$-$T$ plot of the Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ samples with its fitting curves using Eq. (9) is displayed in Fig. 7 and the best-fit parameters of all the samples in the ZFC modes are listed in Table 3. It is noted from Fig. 2(c) that the value of $D$ is found to increase for low irradiation dosage of the 50 kGy sample. With further increase in EB dosage, $D$ is found to decrease. This finding is correlated with the observed behavior of the corresponding cell volume.

The linear part of the inverse susceptibility data above 200 K is fitted using the Curie-Weiss (CW) law which is given by,

$$\frac{H}{M} = \frac{1}{\chi} = \frac{(T - \theta_{CW})}{C}$$

(10)

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_C$ (K)</th>
<th>$T_{ST}$ (K)</th>
<th>$M(0)$ (emu g$^{-1}$)</th>
<th>$b$ (emu K$^{-3/2}$ g$^{-1}$)</th>
<th>$c$ (emu K$^{-5/2}$ g$^{-1}$)</th>
<th>$\mu_{eff}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>161.4</td>
<td>53.0</td>
<td>8.57</td>
<td>-0.0043</td>
<td>$1.9 \times 10^{-5}$</td>
<td>5.1</td>
</tr>
<tr>
<td>50 kGy</td>
<td>162.0</td>
<td>32.3</td>
<td>8.66</td>
<td>-0.0031</td>
<td>$1.2 \times 10^{-5}$</td>
<td>6.1</td>
</tr>
<tr>
<td>100 kGy</td>
<td>162.1</td>
<td>29.9</td>
<td>9.82</td>
<td>-0.0046</td>
<td>$2.1 \times 10^{-5}$</td>
<td>6.2</td>
</tr>
<tr>
<td>200 kGy</td>
<td>161.7</td>
<td>16.2</td>
<td>11.88</td>
<td>-0.0062</td>
<td>$2.8 \times 10^{-5}$</td>
<td>6.7</td>
</tr>
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</table>

Fig. 6. Temperature dependence of magnetization for the pristine and irradiated Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ samples.

Fig. 7. Magnetization fit for the pristine and irradiated Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ samples.
where $\theta_{\text{CW}}$ is the CW temperature and $C$ is the Curie constant. Fig. 8 illustrates the behavior of $H/M$ versus $T$ and it is clearly seen that all samples follow the Curie-Weiss law in the paramagnetic state. The effective magnetic moment $\mu_{\text{eff}}$ can be calculated using the equation
\[
\frac{\mu_{\text{eff}}}{\mu_B} = \frac{3k_B C}{N_A}
\]
where $\mu_B$ is the Bohr magnetron, $N_A$ is the Avogadro's number and $k_B$ is the Boltzmann constant. The values obtained from the fit and the values of effective magnetic moment are tabulated in Table 3.

3.4. Seebeck coefficient

Temperature dependent Seebeck coefficient $S(T)$ of the Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ samples is shown in Fig. 10. It is interesting to note that all samples exhibit only positive $S$ in the entire temperature range of investigation, suggesting that holes are the dominant charge carriers in their thermoelectric transport [56]. The observed $S(T)$ behavior may be attributed to the degree of JT distortion. Under the influence of sufficiently large static JT distortion, the charge carriers normally behave as holes [5,56]. With increasing temperature, the $S$ value smoothly increases as it approaches the characteristic temperature $T_S$ and it starts to decrease above $T_S$. There is a slight upturn trend seen in the low temperature region ($T < 50$ K) which is quite similar to the resistivity data at the low temperatures. Such a behavior could be attributed to the Kondo-like scattering process as we discussed in the electrical resistivity section. In this Kondo region, the charge ordered state may coexist with the dynamics FM clusters as deduced from the ZFC magnetization behavior.

In order to explain the low temperature behavior, we have used theoretical models similar to electrical resistivity in the FM metallic region which is given by
where $S_0$ is a constant, $S_{3/2}T^{3/2}$ is attributed to the magnon drag contribution which strongly influences the low temperature regime and $S_4T^4$ is attributed to the spin wave contribution [6,7,11]. For the presently investigated samples, we fitted the experimental $S(T)$ data with Eq. (13) and found that this model alone cannot describe the $S(T)$ data in the low temperature regime. Therefore, it is plausibly to include a term considering Kondo scattering in Eq. (13). For this reason, we have modified the equation which is given by [12,13],

$$S(T) = S_0 + S_{3/2}T^{3/2} + S_2T^2 + S_3T^3 + S_4T^4$$

(14)

where $S_3T^3$ is due to the contribution of the phonon drag produced by electron-phonon interaction and $S_2T^2$ indicates the contributions due to Kondo-like scattering [12,13]. The $S(T)$ data in the temperature range below $T_S$ was fitted to Eq. (14) and is shown in Fig. 11. We observe that by introducing these additional terms, $S(T)$ behavior can be explained using the model represented by Eq. (14). For example at 150 K, the Kondo term $S_2T^2$ is almost twice as much as the $S_4T^4$ term.

In the high temperature region ($T > T_S$), Seebeck coefficient is mainly governed by polaronic transport since the charge carriers are trapped. As a result, the transport mechanism involves hopping through polarons [12]. Therefore, $S(T)$ in the high temperature region is described by the Mott’s polaron hopping model given by [57].
where $E_s$ is the activation energy, $e$ is the electronic charge, and $\alpha$ is a constant of proportionality between heat transfer and kinetic energy of an electron. Here, $\alpha < 1$ implies the existence of small polarons while for $\alpha > 1$ implies the existence of large polarons. From the slope obtained from the linear fit of the $1/T$ versus $S$ plot as shown in Fig. 11, values of activation energy $E_s$ and $\alpha$ were obtained for all the samples and are tabulated in Table 4. The value of $\alpha$ calculated from the fit is less than unity, suggesting that the thermoelectric transport is dominant by small polarons. It is found that $E_s$ increases with increase in $EB$ dosage upto 100 kGy, then $E_s$ is seen to decrease with further increase in $EB$ dosage. A similar trend is also seen in case of activation energy obtained from resistivity data.

### 3.4.1. Percolation model using Kondo term

Since there is a competition between the two mechanisms in the vicinity of $T_S$, Eqs. (14) and (15) cannot explain clearly the $S(T)$ behavior near $T_S$. Hence, Seebeck coefficient behavior near the transition may be described by the percolation model similar to that in analyzing the electrical resistivity data. The percolation model of $S(T)$ for the entire temperature range can be formulated as [14],

$$ S(T) = S_{FM}^0(T)p + S_{PM}^0(T)(1 - p) $$

where $S_{FM}^0(T)$ and $S_{PM}^0(T)$ are the contributions to $S(T)$ from the ferromagnetic metallic region and the paramagnetic insulating region, respectively, and $p$ is the metallic volume fraction. The volume fraction of paramagnetic and ferromagnetic domains satisfy the Boltzmann distribution,

$$ p = \frac{1}{1 + \exp \left( \frac{\Delta U}{k_B T} \right)} $$

where $\Delta U$ is the energy difference between paramagnetic and ferromagnetic states. Thus, the complete expression for the $S(T)$ in the entire temperature range is rewritten as,
By substituting the value of $p$ in Eq. (18), the $S(T)$ data over the entire temperature range can be analyzed. Fig. 12 shows the percolation fitting curves of $S(T)$ for all the samples and the best-fit parameters are summarized in Table 5. The theoretical and the experimental curves are in good agreement, indicative of the percolative nature of the thermoelectric transport in the Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ system.

$$S(T) = \left( S_0 + S_{3/2} T^{3/2} + S_2 T^2 + S_3 T^3 + S_4 T^4 \right) p$$
$$+ \frac{k_B}{e} \left[ \frac{E_g}{k_B T} + \alpha \right] (1 - p) \tag{18}$$

Table 5
Fitting parameters obtained using percolation fitting of TEP data.

<table>
<thead>
<tr>
<th></th>
<th>Pristine</th>
<th>50 kGy</th>
<th>100 kGy</th>
<th>200 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$ ($\mu$V/K)$^1$</td>
<td>1.9152</td>
<td>1.8839</td>
<td>2.7948</td>
<td>1.6597</td>
</tr>
<tr>
<td>$S_1$ ($\mu$V/K)$^3$</td>
<td>-0.094</td>
<td>-0.0015</td>
<td>-0.169</td>
<td>-0.0711</td>
</tr>
<tr>
<td>$S_2$ ($\mu$V/K)$^4$</td>
<td>2.083</td>
<td>1.362</td>
<td>9.438</td>
<td>5.202</td>
</tr>
<tr>
<td>$S_3$ ($\mu$V/K)$^6$</td>
<td>$-3.1 \times 10^{-5}$</td>
<td>$-9.1 \times 10^{-6}$</td>
<td>$-2.8 \times 10^{-5}$</td>
<td>$-3.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>$S_4$ ($\mu$V/K)$^{10}$</td>
<td>$7.1 \times 10^{-7}$</td>
<td>$2.8 \times 10^{-5}$</td>
<td>$9.1 \times 10^{-7}$</td>
<td>$5.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>$U/(K/k_B)$</td>
<td>$2.8 \times 10^{-20}$</td>
<td>$2.6 \times 10^{-20}$</td>
<td>$2.5 \times 10^{-20}$</td>
<td>$2.9 \times 10^{-20}$</td>
</tr>
<tr>
<td>$T_{S_{\text{mod}}}^{\text{mod}}$ (K)</td>
<td>173.49</td>
<td>190.31</td>
<td>187.78</td>
<td>197.14</td>
</tr>
</tbody>
</table>

3.5. Thermal conductivity

In order to further elucidate other distinct features of these materials, we have also measured the temperature dependent thermal conductivity $\kappa(T)$ in the temperature range of 10–300 K.
and the results are shown in Fig. 13. Since thermal conductivity measurements may provide valuable information about various scattering processes of thermal carriers, the present data would offer an opportunity to probe the interplay between various scattering processes. It should be mentioned here that the measured values of $\kappa (300 \text{ K})$ are small and are comparable to that of other perovskite manganites [6,46,48]. For a crystalline solid, such a low value of thermal conductivity can be originated from various kinds of disorders present in the lattice. Comparing thermal conductivity data of various perovskites manganites [6,46,48], such a scenario can be attributed to the vibronic interactions of Mn$^{3+}$ (Jahn-Teller) ions, which critically limit the mean free path of phonons.

At low temperatures, $\kappa (T)$ increases with temperature and a maximum appears around 30 K for all the samples. Such an observation is a typical feature for the reduction of thermal scattering in solids at low temperatures [48]. The small peak value of thermal conductivity is observed for all the samples at characteristic temperature $T_a$, below 35 K which is an induction of the crossover from Umklapp scattering to defect limited scattering. With further increase in temperature, $\kappa$ decreases with temperature essentially due to the enhanced phonon-phonon scattering [37,47,48]. It is well-known that the total thermal conductivity is a sum of the electronic and lattice contributions. It can be expressed as $\kappa (T) = \kappa_e(T) + \kappa_l(T)$, where $\kappa_e$ is the contribution of electronic thermal conductivity and $\kappa_l$ is due to lattice contributions. The electronic thermal conductivity $\kappa_e$ can be evaluated using the standard Wiedemann-Franz (WF) law which is given by, $\kappa_e(T) / L = \frac{\rho(T)}{T}$, where $\rho(T)$ and $L$ (=2.45 x 10$^{-8}$ W K$^{-2}$) are the electrical resistivity of samples and the Lorenz number, respectively. For the presently investigated samples the estimated electronic thermal conductivity ($\kappa_e$) contribution from the Wiedemann-Franz law is much smaller as compared to the total thermal conductivity. Consequently, the predominant contribution to the measured $\kappa$ comes from the lattice thermal conductivity ($\kappa_l$) with a negligibly small contribution of $\kappa_e$. In the high-temperature insulating state, it can be clearly seen from Fig. 13 that $\kappa$ displays a characteristic of phonon scattering (d$\kappa$/dT > 0), which is usually observed in amorphous solids. Such an observation is similar and comparable in magnitude to the case of hole-doped manganites [49,58]. Usually the high-$T$ thermal conductivity of the crystalline insulators is mostly a decreasing function of temperature and the observed increasing function of $\kappa (T)$ cannot be attributed to high-temperature electron or phonon processes. Such an unusual behavior of $\kappa (T)$ at high temperatures may be attributed to the local anharmonic lattice distortions associated with small polars [59], in accordance with the present electrical resistivity and the Seebeck coefficient results. Moreover, to have a quantitative view of the small polarons transport, $\kappa (T)$ can be expressed as the following equation,

$$\kappa (T) = \kappa_0 \exp \left( \frac{T}{T} \right)$$  (19)

where $\kappa_0$ and $T$ are the fitting parameters and the obtained values for all samples are listed in Table 6. It is found that $T$ increases with increasing dosage of EB irradiation, a direct consequence of the degree of local anharmonic lattice distortions associated with small polars in the high temperature region.

Table 6: The parameters obtained from thermal conductivity and specific heat data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pristine</th>
<th>50 kGy</th>
<th>100 kGy</th>
<th>200 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_0$ (W/m K)</td>
<td>2.9879</td>
<td>2.7563</td>
<td>2.6879</td>
<td>2.2479</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>1223.7</td>
<td>1365.6</td>
<td>1556.6</td>
<td>2222.7</td>
</tr>
<tr>
<td>$\Delta S$ (J/mol K)</td>
<td>0.2246</td>
<td>0.1952</td>
<td>0.1476</td>
<td>0.1459</td>
</tr>
<tr>
<td>$T_{cv}$ (K)</td>
<td>151.5</td>
<td>153.9</td>
<td>155.8</td>
<td>157.2</td>
</tr>
</tbody>
</table>

3.6. Specific heat

Fig. 14 shows the temperature dependence of specific heat ($C_p$) for the pristine and irradiated Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ compounds in the temperature range of 80–300 K. For each sample, a weak hump around the characteristic temperature denoted by $T_{cp}$ is identified. From the high resolution specific heat measurements, it was revealed that the transition temperature $T_{cp}$ increases slightly with EB irradiation (see inset of Fig. 14). The specific heat jump ($\Delta C_p$), near the transition was estimated by subtracting a smooth lattice background fitted far away from the transitions. The change in entropy $\Delta S$ associated with the FM transition is calculated in order to separate the lattice contribution and to obtain the excess specific heat due to magnetic ordering. It can be obtained by integrating the area under $\Delta C_p/T$ versus $T$ curve (inset of Fig. 14). This plot assumes that $S=0$ at $T=0$ (known as zero point entropy) [60]. The estimated values of $\Delta S$ together with the corresponding $T_{cp}$ are listed in Table 6. It is noted that the present result of pristine sample is in fair agreement with those reported for some of the similar class of materials [6,7,46]. It is noted that a considerable reduction in the value of $\Delta S$ is observed with increasing EB dosage, indicating an increase in magnetic inhomogeneity in the EB irradiated samples [7].

4. Conclusions

The XRD studies show that pristine as well as EB irradiated Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ samples are single phased and crystallize in orthorhombic symmetry with Pbnm space group. The lattice parameters initially decrease for lower EB dosage (up to 50 kGy), however an increase in lattice parameters is observed for dosages beyond 50 kGy. The EB irradiation also causes an increase in bond angle which enhances charge ordering due increase in distortion in the system. The conduction mechanism in the insulating region can satisfactorily explained using SPH model and the metallic region can be explained using a theory based on Kondo-like spin dependent scattering and other electron scattering mechanisms. The electrical transport mechanism in the entire temperature range has been effectively elucidated using the percolation model.
All the samples exhibit a FM-PM transition and $EB$ irradiation seems not to have an appreciable effect on $T_C$. Mechanism responsible for Seebeck coefficient at high temperatures was explained using SPH model and the low temperature anomalous S(T) behavior has been described using a theory based on the Kondo effect and electron-electron and electron-phonon interaction. Specific heat measurement clearly indicates that $EB$ irradiation effectively increases the magnetic inhomogeneity of the Pr$_2$Sr$_2$MnO$_6$ system.

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References