Enhancement of temperature coefficient of resistance (TCR) and magnetoresistance (MR) of La$_{0.67-x}$RE$_x$Ca$_{0.33}$MnO$_3$ ($x = 0, 0.1$; RE = Gd, Nd, Sm) system via rare-earth substitution

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Abstract
We investigated the influence of 10% substitution of rare-earth (RE) elements on the crystallographic, transport, and magnetic properties of La$_{0.67-x}$RE$_x$Ca$_{0.33}$MnO$_3$ (RE = Nd, Sm, and Gd, $x = 0, 0.1$) manganite perovskite compounds. The bulk polycrystalline samples were synthesized using solid-state reaction method. The phase purity and crystal structure of studied samples were confirmed by room temperature X-ray diffraction followed by the Rietveld refinement analysis. A high temperature insulator to low temperature metal phase transition is observed in electrical transport measurement. We observed an enhancement in the temperature coefficient of resistance (TCR) and magnetoresistance (MR) by partially substituting La with RE ions. The maximum $TCR \approx 22\%$ and MR $\approx 96\%$ are observed in Gd doped sample. The magnetic transition temperature, $T_c$, decreases from $\sim 254\, K$ for the pristine sample to about $\sim 165\, K$ for the Gd-doped sample. Our analysis of electrical and thermal transport data shows that the Small Polaron Hopping (SPH) is predominant at high temperatures conduction mechanism, whereas at low temperatures mechanism is dominated by electron-magnon scattering. The high temperature insulator paramagnetic phase to low temperature metallic ferromagnetic phase transitions are also observed in thermal conductivity and specific heat.

1. Introduction

In recent years, the physiochemical properties of perovskite manganite oxides with a general formula $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ (RE = trivalent lanthanide rare-earths, and A = Ca$^{2+}$ or Sr$^{2+}$) have been extensively investigated [1–5]. These materials show a variety of fascinating physical properties, including colossal magnetoresistance (CMR), insulator-metal transitions, and magneto-caloric effect (MCE) [5–7]. These properties make manganese perovskites potential candidates for magnetic recording devices, magnetic actuators, and sensors [8–11]. The intriguing physical properties result from the strong electron correlations and strong electron-lattice coupling, known as Jahn-Teller interaction [1,12–14]. A delicate tuning of spin, orbital, lattice and charge degrees of freedom may cause a modification in electron correlations and electron-lattice coupling and result in a significant alteration in the magnetoelectronic properties of these materials.

Among all the perovskite manganites, the calcium doped La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) compound has been studied extensively owing to their significant temperature coefficient of resistance (TCR) and magnetoresistance (MR) [3,14]. The large value of TCR and MR in LCMO compounds make them excellent candidates for storage devices, magnetic sensors, and bolometers applications. In addition to these applications, LCMO materials are also used in devices such as laser energy meter, infrared detectors, and solid oxide fuel cells [15,16]. However, these functional properties are observed slightly lower than room temperature. Various attempts, such as...
substitution at La and Mn sites with isovalent and heterovalent elements and different synthesis methods, have been used to improve or alter the TCR, MR, and other physical properties of La0.67Ca0.33MnO3 system [17–19]. It has been observed that the intrinsic properties such as MR of mixed-valence perovskite manganites can be influenced dramatically by extrinsic property like grain size [20]. Another way to alter the physical properties of these materials is by partial substitution of La by isovalent rare earth, i.e., Pr3+, Eu3+, Sm3+, Gd3+, Y3+ etc. Out of many external stimuli used to control and manipulate the physical properties of these materials, controlled chemical doping is considered the most efficient technique. The small ionic size rare-earth substitution produces the chemical pressure in the unit cell and hence deforms the MnO6 octahedra. The deformation of MnO6 octahedra results in a significant change in the Mn–O–Mn bond angle subsequently modifies the one-electron bandwidth [2, 21].

For practical applications, TCR and MR are vital parameters, and numerous efforts have been made to enhance these parameters. In the literature, there is relatively less work has been reported on the effect of RE substitution connected to the TCR, magnetotransport and thermal transport properties in La0.67Ca0.33MnO3 system. In the present work, efforts have been made to improve the TCR and MR values of the LCMO system with by a partial substitution of La by smaller ionic radii rare-earth elements. The magnetic and thermal properties have also been investigated for the same. In this communication, we report a systematic study of structural, electrical, magnetotransport, and thermal properties of the La0.67–xRExCa0.33MnO3(RE = Nd, Sm, and Gd, x = 0.0, 0.1) system.

2. Experimental details

The bulk polycrystalline samples were prepared by solid-state reaction technique using high purity (≥ 99.9%) commercially available powder of La2O3, Mn2O3, CaCO3, and RE2O3 (RE = Nd, Sm and Gd). The precursors were taken in stoichiometric ratio and milled 6 h in agate mortar-pestle. The milled powder was calcinated at various temperatures of 900 °C, 1100 °C, and 1200 °C for 24 h, each with intermediate grindings to promote the sample homogeneity. Finally, the calcinated powder was pelletized in a rectangular shape and sintered at 1300 °C for 48 h, followed by natural cooling of the furnace. The room temperature X-ray diffraction (XRD) was used to confirm the crystal structure and phase purity of the studied compounds. The Rietveld refinement technique is employed using an open-source FullProf program to estimate the structural parameters. Electrical transport measurements were carried out using a standard four-probe method in Physical Properties Measurement Systems (PPMS-9 T). A 9 Tesla PPMS based vibrating sample magnetometer (VSM) was used for magnetic measurements. A heat-pulse technique was used on a closed cycle refrigerator carry out the Seebeck coefficient (S) and thermal conductivity (κ) measurements. Heat capacity measurements were performed using a high-resolution ac calorimeter.

3. Results and discussions

3.1. Structural properties

The Rietveld fitted room temperature XRD data for all the studied samples are shown in figure 1. An explicit agreement between the experimental and the theoretically simulated data can easily visualize from figure 1. No new peak of any impurity phase has been observed within detectable limits of the instrument. The Rietveld refined lattice parameters and the value of other fitting parameters, which quantifies the quality of refinement of the samples, are tabulated in table 1. The visual inspection of figure 1 and close to one value of χ² (including reasonably acceptable values Rw, Rw%) indicates that the samples are in a single phase.

Rietveld analysis reveals no influence of RE-doping at A-site on crystal symmetry. The doped compounds possess a similar orthorhombic crystal structure (with the Pbnm space group) as pristine. However, unit cell parameters and volume decrease systematically with the 10% substitution of La by lower RE ionic radii. As Nd, Sm, and Gd are isovalent to La, partial substitution of these elements does not introduce any extra charge. However, the effective average ionic radii (〈rA〉) of A-site (La0.67–xRExSr0.33) decreases monotonically with reduced ionic radii of RE-elements. The change in the 〈rA〉 distort the MnO6 octahedra which prominently influences the physical properties of these materials. The RE substitution enhances the Jahn-Teller (J − T) distortion in the manganese octahedral [4, 13].

The orthorhombic structure can be quantitatively described using orthorhombic deformation (D(%) = (222)).

\[
D(%) = \frac{1}{3} \sum_{i=1}^{3} \left| \frac{a_i - \bar{a}}{\bar{a}} \right| \times 100
\]
Figure 1. Rietveld refined room temperature X-ray diffraction data of (a) La$_{0.67}$Ca$_{0.33}$MnO$_3$ (b) La$_{0.57}$Nd$_{0.1}$Ca$_{0.33}$MnO$_3$ (c) La$_{0.57}$Sm$_{0.1}$Ca$_{0.33}$MnO$_3$ and (d) La$_{0.57}$Gd$_{0.1}$Ca$_{0.33}$MnO$_3$ samples. The observed intensities are shown as dots, calculated by red solid line, allowed Bragg position by green vertical lines and the difference between the experimental and refined patterns by bottom blue line.

Table 1. Summary of Rietveld refined structural and goodness of fit parameters for the studied samples.

| Sample name     | Pristine         | Nd = 0.1          | Sm = 0.1         | Gd = 0.1         |
|-----------------|------------------|-------------------|------------------|------------------|
| System          | orthorhombic     | orthorhombic      | orthorhombic     | orthorhombic     |
| Space Group     | Pbnm             | Pbnm              | Pbnm             | Pbnm             |
| a (Å)           | 5.474(9)         | 5.459(5)          | 5.452(1)         | 5.442(9)         |
| b (Å)           | 5.461(7)         | 5.455(3)          | 5.452(2)         | 5.449(4)         |
| c (Å)           | 7.715(7)         | 7.703(2)          | 7.706(2)         | 7.712(1)         |
| c/√2 (Å)        | 5.455(8)         | 5.447(0)          | 5.449(1)         | 5.453(3)         |
| α = β = γ       | 90.00            | 90.00             | 90.00            | 90.00            |
| V (Å$^3$)       | 230.71(7)        | 229.43(0)         | 229.07(1)        | 228.74(7)        |
| Rp              | 3.11             | 3.45              | 3.22             | 3.2              |
| Rp'             | 4.08             | 4.49              | 4.23             | 4.22             |
| Rwp             | 4.02             | 4.05              | 3.96             | 3.71             |
| χ²              | 1.03             | 1.23              | 1.14             | 1.29             |
| D (%)           | 0.1315(4)        | 0.0850(4)         | 0.0244(7)        | 0.0688(9)        |
| t               | 0.9175           | 0.9156            | 0.9145           | 0.9136           |
| δ(δ(0) Å)       | 1.9602(2)        | 1.9604(8)         | 1.9619(7)        | 1.9650(2)        |
| ω(°)            | 160.8695         | 159.064           | 159.547          | 159.5335         |
| W               | 0.0935(1)        | 0.0932(1)         | 0.0930(3)        | 0.0925(3)        |
where $a_1 = a$, $a_2 = b$, $a_3 = c/\sqrt{2}$, and $\bar{a} = (abc/\sqrt{2})^{1/3}$. The estimated values of orthorhombic deformation are presented in table 1. The $D$ values for all pure and doped samples are of the order of 0.1%, suggesting that the substitution of smaller radii rare-earth elements at La site has little influence on crystal symmetry.

In terms of ionic radii, Goodenough tolerance factor widely used parameter to determine the degree of distortion in the ABO$_3$ perovskite manganites [15]. The tolerance factor is expressed as,

$$
\bar{t} = \frac{\left(r_A\right) + r_O}{\sqrt{2} \left(r_B\right) + r_O},
$$

(2)

Where $\langle r_A \rangle$ and $\langle r_B \rangle$ are the average ionic radii of the A-site, B-site and $r_O$ is the radii of oxygen ion, respectively. The average ionic radius with nine coordination for A-site cation and 6 for the oxygen ion is used to calculate the tolerance factor. Table 1 presents the $\bar{t}$ values for all the samples. The $\bar{t}$ values decrease from 0.917 to 0.913 (see table 1) with the decrease in RE cationic radius, which indicates an increment in Mn–O bond length and thus reduction in single electron bandwidth ($W$).

The identification of structural deformation of A-site doped samples is characterized by the bond length and bond angle between oxygen and manganese ions, shown in table 1. It can be seen from table 1, the Mn–O bond length ($d_{\text{Mn-O}}$) increases monotonically as the ionic radius of RE ions decreases, whereas Mn–O–Mn bond angles ($\omega$) decreases slightly. The change in Mn–O bond length and bond angle effectively change the one-electron bandwidth $W$ (electron hopping interaction), one of the crucial parameters for manganite physics. The one-electron bandwidths ($W$) for the studied materials are estimated using an empirical formula [2, 17],

$$
W \approx \cos \left( \frac{\omega}{2} \right) \frac{d_{\text{Mn-O}}^{3.5}}{d_{\text{Mn-O}}}.
$$

(3)

Here, $d_{\text{Mn-O}}$ represent the bond length between Mn$^{3+}$ and O$^{2-}$ ions and $\omega$ symbolizes the Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ bond angle. The estimated values of $W$ are also tabulated in table 1. The values of $W$ decreases with decreasing the average ionic radius of A-site. The decrease in the one-electron bandwidth ($W$) suggests that the double exchange (DE) interaction plays a dominating role as compared to super-exchange interactions or other electronic instabilities [2].

### 3.2. Electrical resistivity

The electrical resistivity as a function of temperature and applied magnetic field (0 T, and 9 T) are shown in figures 2(a) and (b). The pristine, as well as doped samples, demonstrate high temperature insulator to low temperature metal transition with and without the applied magnetic field. The insulator-metal transition temperature ($T_{IM}$) is monotonously decreased from 262 K to 183 K as the effective ionic radii of A-site (La$_{0.67-x}$RE$_{x}$Ca$_{0.33}$) decreases. The estimated values of $T_{IM}$ are presented in table 2. The electrical resistivity for the doped compounds found to be higher in comparison to the pristine compound in the studied temperature range. The enhancement in the resistivity ascribed to the distortion of MnO$_6$ octahedra and the enhancement of the magnetic domain scattering. As the resistivity is found to be less in Sm doped sample compare to Nd and Gd doped samples, it suggests that the magnetic domain scattering has more influence on overall resistivity enhancement [20, 23].
We exploited different theoretical models related to electron conduction to unravel the electrical transport mechanism of the studied samples. At high temperatures ($T > T_{IM}$), the resistivity shows an insulating behavior for all the samples, which can be described by a small polaron hopping model (SPH) [24, 25]. According to SPH model, the temperature dependent electrical resistivity is given by,

$$\rho_{SPH}(T) = AT \exp(E_A/k_B T)$$  \hspace{1cm} (4)

Where $E_A$ is the thermal energy required to polaron for site jumping, $T$ is the absolute temperature, $A$ is a prefactor which is given by $A = 2k_B/3ne^2\nu$, here, $k_B$ is Boltzmann constant, $n$ is the number of charge carriers, $\nu$ is the longitudinal optical phonon frequency, $e$ is electronic charge, and $a$ is hopping distance. The resistivity data fitted with equation (4) are shown in figure 3(a) and the obtained parameters are listed in table 2.

![Figure 3. A plot of resistivity versus temperature for $La_{0.67-x}RE_{x}Ca_{0.33}MnO_3$($RE = Nd, Sm, and Gd, x = 0.0, 0.1$) samples fitted with various models. (a) The high temperature black dotted line represents the best fit to the SPH model (equation (4)) and black solid line in low temperature shows the best fit curve using equation (5). (b) The solid lines represent the best fits according to equation (6).](image)

The low-temperature ferromagnetic region transport mechanism of manganites usually depends on the combination of electron-electron, electron-phonon, and electron-magnon scattering process in the ferromagnetic state [27]. The resistivity data fitted with equation (5) are shown in figure 3(a). The obtained values of $\rho_0, \rho_2, T^2$, and $\rho_{4.5}$ are presented in table 2. The fits show that the contribution $\rho_2 T^2$ term is much more significant than the $\rho_{4.5} T^{4.5}$ term in resistivity data indicates that the electron-electron scattering dominates the low-temperature conduction mechanism.

To get a more in-depth insight into the electronic conduction mechanism in studied materials, the resistivity data were analyzed using a phenomenological percolation model in the full temperature range. According to the percolation model, the competing $FM$ and $PM$ phases coexist in the material [28] and their volume fraction

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**Table 2.** Values of various fitting parameters obtained from the temperature dependent electrical resistivity of $La_{0.67-x}RE_{x}Ca_{0.33}MnO_3$($RE = Nd, Sm, and Gd, x = 0.0, 0.1$) samples.

| Sample     | $T_{IM}$ (K) | $\rho_0$ ($\Omega \cdot mm$) | $\rho_2 \times 10^{-6}$ ($\Omega \cdot mm/K^2$) | $\rho_{4.5} \times 10^{-12}$ ($\Omega \cdot mm/K^{4.5}$) | $E_A$ (meV) | $A \times 10^6$ | $T_{C_{Mod}}$ (K) | $U_0/k_B$ (K) |
|------------|--------------|-------------------------------|-----------------------------------------------|-----------------------------------------------|-------------|----------------|------------------|---------------|
| Pristine   | 265.13       | 0.01236                        | 0.6545                                        | 1.6258                                        | 152.0159    | 0.916          | 257.182          | 18624.84      |
| Nd = 0.1  | 228.45       | 0.96816                        | 79.7394                                       | 87.5486                                       | 153.096     | 14.923         | 228.142          | 15706.85      |
| Sm = 0.1  | 195.77       | 0.02517                        | 0.3189                                        | 24.2053                                       | 135.211     | 2.942          | 186.315          | 12355.50      |
| Gd = 0.1  | 185.63       | 0.40579                        | 7.01259                                       | 364.654                                       | 144.414     | 8.227          | 181.811          | 5236.99       |
varies with temperature. The temperature-dependent resistivity according to percolation theory can be written as,

\[ \rho(T) = \rho_{\text{FM}} f + \rho_{\text{PM}} (1 - f) \]

where, \( f \) and \( 1 - f \) are the volume fractions of ferromagnetic and paramagnetic domains, respectively. The volume fraction ferromagnetic domains in the paramagnetic region (or vice versa) follows the Boltzmann distribution,

\[ f = \frac{1}{1 + \exp(\frac{\Delta U}{k T})} \]

where, \( \Delta U = -U_0 (1 - \frac{x}{x_{\text{mode}}}) \) is an activation energy barrier of insulating and metallic states. The \( T_{\text{c-mode}} \) and \( U_0 \) are used as a free parameters to comprehend the best fit. The \( \rho_{\text{PM}} \) and \( \rho_{\text{FM}} \) keep fixed to the values obtained from the independent fittings. The fitted curve of resistivity to equation (6) are shown in figure 3(b) and yielded parameters are given in table 2. Equation (6) fits reasonably well to the experimentally observed resistivity data in the whole temperature range, which suggests that the electrical conduction mechanism can be explained by the percolation model, satisfactorily.

3.3. Temperature coefficient of resistance (TCR)
The temperature coefficient of resistance (TCR) is one of the vital for the integration of these materials in bolometric and infrared detectors [29, 30]. The estimated values of TCR as a function of temperature are plotted in figure 4. The pristine sample of Lao.67Ca0.33MnO3 shows a TCR value \( \sim 9\% \), which is in good agreement with reported literature [31]. The Nd-doped sample shows a maximum TCR of around \( \sim 11\% \) at 212 K. The TCR values are reduced with Sm-doping with the maximum TCR value of about 6% at 166 K. Remarkably, the Gd-doped sample possesses a TCR value of nearly 22% at 175 K. We thus conclude that Gd is the best dopant among the various RE-doped samples. In general, thin films display higher TCR values as compared to that of their bulk counterparts. Hence, it would be interesting to prepare thin films of Gd-doped samples, and we anticipate that such films should have high TCR values.

3.4. Magnetoresistance (MR)
The magnetoresistance (MR) for the studied sample was calculated using a relation; \( \text{MR} = \frac{R(0) - R(H)}{R(0)} \), where \( R \) (0) and \( R(H) \) are respectively the resistivities in zero field and applied magnetic field (9 T in present case). The estimated MR (%) for pure and doped samples are shown in figure 5. The external applied magnetic field reduced the resistivity significantly (see figure 2(b)), indicating that the applied magnetic field enables electrons hopping between the adjacent Mn ions. This observation is consistent with the DE model [2, 32]. It is evident from figure 5 that below \( T_{\text{IM}} \) magnetoresistance is directly proportional to temperature, whereas, above \( T_{\text{IM}} \) it behaves oppositely.
The MR values at transition temperature are found to be 86% for pristine sample, 81% for Nd-doped, 96% for Sm-doped, and 94% for Gd-doped samples. The observed values magnetoresistance in the studied materials considerably higher than the reported values of MR in Sm_{0.7}Ca_{0.3}MnO_{3} (22% at 77 K) and Nd_{0.7}Ca_{0.3}MnO_{3} (32% at 110 K) [33]. Our analysis suggests that structural distortion may be the key parameter governing the CMR response. The doping on La site enhances the distortion in the MnO_{6} octahedra and consequently increases the MR values. Two factors may lead to higher magnetoresistance viz. (a) the higher resistivity at low temperatures and (b) reduced carrier mobility. Both factors can be depending upon the electronic bandwidth, which can tune by bending of Mn–O–Mn bond angle [34]. The external magnetic field force the alignment of magnetic domains in the same directions, which ease the electron hopping across the domain wall. The easier electron hopping enhances the conductivity, which leads to a significant increase in MR at low temperatures.

3.5. Magnetic properties

The evolution of the magnetic phase for pure and doped samples is investigated in both zero-field-cooled (ZFC) and field-cooled (FC) protocols. The magnetization as a function of temperature were recorded at 100 Oe applied magnetic field are shown in figures 6(a)–(c). All the sample shows a phase transition from high temperature paramagnetic state (PM) to low temperature ferromagnetic (FM) state. A low temperature ferromagnetic state can be well recognized by the bifurcation between FC and ZFC curves. For better estimation of the transition temperature (T_{c}), we used points of inflection dM/dT versus T curves, as shown in the insets of the respective figure of figure 6. The estimated values of T_{c} values are listed in table 3.

Magnetic measurement shows that T_{c} is directly proportional to the ionic radii of RE. The T_{c} decreases as the ionic radius of RE decreases. The observed values of T_{c} are found to be slightly higher than T_{IM}, which is consistent with the earlier observation for manganites [32, 35]. The pristine sample has the highest value of T_{c} and T_{IM} of about 255 K and 265 K, respectively. The paramagnetic susceptibility is analyzed using Curie-Weiss law to obtained the effective magnetic moments and to understand the magnetic interactions in the studied materials. According to Curie-Weiss law, the inverse susceptibility (\chi^{-1} = H/M) in the paramagnetic region is expressed as,

\[
\frac{1}{\chi} = \frac{T - \theta_{W}}{C},
\]

where C is Curie constant, and \theta_{W} is the Curie-Weiss temperature. The studied samples exhibit linear behavior above 200 K, as shown in figures 6(d)–(f). The little deviation from the linear behavior of inverse susceptibility may be due to the coexistence of inhomogeneous magnetic phases [6, 36–38]. The estimated values of Curie-Weiss temperature (\theta_{W}) and effective magnetic moments (\mu_{eff}) from the linear fit of inverse susceptibility are given in table 3.

The Curie-Weiss temperature is directly related to the exchange integral of the magnetic system. The substitution of A site by smaller ionic radii element induced the lattice distortion and consequently total...
exchange integral, which in turn change the Curie-Weiss temperature \[ \theta_W \] revealed in studied samples. To estimate the \( \mu_{\text{eff}} \) for these samples, we utilize the standard expression for \( C \), which is given by

\[
m = CNk_B^3\mu_{\text{eff}}^2 AB
\]

where \( N_A \) is Avogadro number, \( k_B \) is the Boltzmann constant and \( \mu_{\text{eff}} \) is the experimentally observed effective magnetic moment. The estimated values of \( \mu_{\text{eff}} \) from temperature dependent paramagnetic susceptibility data are compared with the theoretically estimated values. The theoretical values of \( \mu_{\text{eff}} \) are calculated using the following formula [39],

\[
\mu_{\text{eff}}^{\text{cal}} = [(1 - x)\mu_{\text{eff}}^{\text{RE}} + (1 - x)\mu_{\text{eff}}^{\text{Mn}^{3+}} + x\mu_{\text{eff}}^{\text{Mn}^{4+}}]^{1/2},
\]

where, \( \mu_{\text{eff}}^{\text{RE}} \) , \( \mu_{\text{eff}}^{\text{Mn}^{3+}} \) and \( \mu_{\text{eff}}^{\text{Mn}^{4+}} \) represents the effective magnetic moment of rare-earth (RE\(^{3+}\)), and the Mn\(^{3+}\) and Mn\(^{4+}\) ions, respectively. The effective magnetic moments of Mn\(^{3+}\) and Mn\(^{4+}\) ions are taken as 4.90 \( \mu_B \) and 3.78 \( \mu_B \), respectively [40]. The observed and calculated values of effective magnetic moments are

Figure 6. Temperature dependent magnetization curves of (a) La\(_{0.67}\)Ca\(_{0.33}\)MnO\(_3\) (b) La\(_{0.57}\)Nd\(_{0.1}\)Ca\(_{0.33}\)MnO\(_3\) (c) La\(_{0.57}\)Gd\(_{0.1}\)Ca\(_{0.33}\)MnO\(_3\) samples measured under 100 Oe applied magnetic field in both ZFC and FC conditions. Insets show the \( dM/dT \) versus \( T \) curve for the corresponding samples. Right panel shows the temperature dependence of the inverse paramagnetic susceptibility fitted to the equation (8) for studied compositions.

### Table 3: Curie temperature (\( T_c \)), Curie constant (\( C \)), Curie-Weiss temperature (\( \theta_W \)) and magnetic moment \( \mu_{\text{eff}} \) (observed and calculated) from magnetization data La\(_{0.67-x}\)RE\(_x\)Ca\(_{0.33}\)MnO\(_3\) (RE = Nd and Gd, \( x = 0.0, 0.1 \)) samples.

| Sample          | \( T_c \) (K) | \( C \) | \( \theta_W \) (K) | \( \mu_{\text{eff}}^{\text{cal}} \) (\( \mu_B \)) | \( \mu_{\text{eff}}^{\text{obs}} \) (\( \mu_B \)) |
|-----------------|---------------|--------|-------------------|-----------------------------------------------|-----------------------------------------------|
| Pristine        | 255.438       | 3.1037 | 265.6551          | 4.9829                                        | 4.6152                                        |
| Nd = 0.1        | 218.634       | 3.8179 | 252.9289          | 5.5266                                        | 4.7551                                        |
| Gd = 0.1        | 167.045       | 5.0877 | 213.8884          | 6.3798                                        | 5.254                                         |

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tabulated in table 3. The higher values of $m_{\text{eff}}^{\text{obs}}$ in compare to $m_{\text{eff}}^{\text{cal}}$ can be ascribed to the existence of the FM state above $T_c$ \cite{37, 38}.

3.6. Seebeck coefficient

The measured Seebeck coefficient ($S$) as a function of temperature for all the studied samples is depicted in figure 7. All the studied samples shows negative values of $S$ at room temperature. However, the low-temperature behavior is significantly different for the pristine and doped samples. The Seebeck coefficient is negative for the undoped sample except in the temperature range from 100 K to 200 K, with a minimum of around 60 K. At the phase transition, a sharp change of slope in $S$ is observed. On the contrary, all the doped samples show a sharp positive peak in the Seebeck coefficient near transition temperature, and the $S$ values remain positive down to the lowest measured temperature.

The Seebeck coefficient changes the sign from positive to negative at about 250 K, 263 K, and 234 K for Nd, Sm, and Gd-doped samples, respectively. The changing sign of $S$ suggests that two different types of charge carriers coexist in the system. The sign reversal in the Seebeck coefficient is commonly observed in the hole-doped semiconductors. The negative value of $S$ at higher temperatures is expected due to the higher mobility of electrons. As the temperature decreases, the effective bandgap becomes wider, and the negative contribution from electrons to the Seebeck coefficient becomes smaller \cite{41, 42}. All samples show a broad peak with temperature, which can be ascribed due to the rise in the electron-magnon scattering with temperature.

To elucidate the thermoelectric transport of the studied materials, the $S - T$ curves are analyzed according to well-known Mott and Davis adiabatic small polaron conduction theory \cite{43}. According to Mott-Davis theory, the high-temperature Seebeck coefficient is given by,

$$S = \frac{k_B}{e} \left( \frac{\Delta}{k_B T} + \alpha \right)$$

Where $\Delta$ represents activation energy of the charge carriers, $k_B$ is Boltzmann constant, $e$ is charge of electron, $T$ is absolute temperature, and $\alpha$ is related to the entropy of the charge carriers. The value of $\alpha$ is an important parameter to understand the nature of the quasi-particle responsible for the conduction mechanism. Generally, $\alpha$ value is higher than one for large polaron and less than one for small polaron hopping \cite{24, 43}. The measured and fitted data are shown in figure 8(a).

The obtained activation energies and $\alpha$ values for the studied samples are listed in table 4. The smaller values of $\alpha$ suggest that the small polaron hopping is playing a prominent role in the conduction mechanism of studied samples. In the low-temperature ferromagnetic metallic region, the Seebeck coefficient is analyzed using the following relation \cite{44},
accounts for the electron-magnon scattering contributions, and the last term, $g$, where $K = \omega - \omega'$, is more significant than the $S_T/2$ term.

The observed and fitted curves are shown in figure 8(b) and yielded parameters tabulated in table 4. In the fitting temperature range, the contribution from the $S_T/2$ term is more significant than the $S_T T^4$ term, which indicates that the electron–magnon scattering mechanism dominates the low-temperature thermoelectric transport.

### 3.7. Thermal conductivity

Figure 9 depicted the thermal conductivity, $\kappa$, of the $La_{0.67-}RE_{x}Ca_{0.33}MnO_3$ compounds in the temperature range 10–300 K. All the studied samples exhibit a step-like anomaly (pointed by arrows in figure 9) around $T_{IM}$, below which $\kappa$ increases with decreasing the temperature, and a broad peak appears near 40 K, below which the value of $\kappa$ decreases sharply. The sharp decrease in $\kappa$ is attributed to the reduction in the thermal scattering at lower temperatures, and the appearance of the peak in $\kappa$ around 40 K is as a result of enhanced phonon–phonon scattering (Umklapp processes). Near room temperature, the overall values $\kappa$ varies in the range 20–25 mW/cm-K for presently studied samples. Such a low value of thermal conductivity indicates the existence of the Jahn-Teller distortion in the studied samples [45]. The magnitude of low-temperature peak gets suppressed monotonically with the substitution of La by lower radii rare-earth element, suggesting the destabilization of the Jahn-Teller distortion for the smaller ionic radii substitution [46]. The thermal conductivity of magnetic materials is usually described by $\kappa_{tot} = \kappa_{latt} + \kappa_{ele} + \kappa_{mag}$, where $\kappa_{latt}$, $\kappa_{ele}$, and $\kappa_{mag}$ are contribution due to the phonon, electron, and magnons, respectively. The third term is applicable in the magnetically ordered state; therefore, above $T_c$, the third term can be neglected, i.e., $\kappa_{mag} \approx 0$. The electronic contribution of the thermal conductivity is calculated using Wiedemann–Franz law, $\kappa_{ele} = \sigma LT$. Here, $\sigma$ is the electrical conductivity, $L$ is a Lorenz number ($L = 2.45 \times 10^{-8}$W/K²), and $T$ is an absolute temperature [47].

Our analysis suggests that the electronic contribution to the total thermal conductivity is less than 1% in all the samples. Therefore, we conclude here that phonon plays a dominant role in the measured thermal conductivity rather than charge carriers.

$$S_T = S_0 + S_{T/2} T^{3/2} + S_T T^4$$  \hspace{1cm} (11)
3.8. Specific heat

Figure 10 displays the temperature variation of specific heat \( C_p \) for pure and RE-doped samples. The absolute value of \( C_p \) at 300 K is around 113 J/mol-K, which is comparable to the other reports in the literature [48, 49]. The specific heat decreases continuously with decreasing temperature. In all the studied samples, specific heat \( C_p(T) \) shows a peak corresponding to the paramagnetic insulating phase to ferromagnetic metallic phase.

The transition temperature of \( C_p \) decreases with the decrease in ionic radii of the doped RE elements, and the transition temperature determined from specific heat measurements matches very well with the magnetic measurements. It is noted that the peak height is actively suppressed from the pure to Gd-doped samples. For a better view of the anomalous feature in the vicinity of \( T_c \), we plotted \( C_p(T) \) versus \( T \) for the doped samples in the inset of figure 10. A small peak in specific heat corresponding to the ferromagnetic-paramagnetic transition can be seen in the inset. The observed suppression and broadening of the \( C_p \) peak suggest a significant increase in the magnetic inhomogeneity as a result of the substitution of RE at the La site for the \( \text{La}_{0.67} \text{Ca}_{0.33} \text{MnO}_3 \) compound.
The magnetic inhomogeneity could be due to the increase of the disorder or coexistence of the magnetic phases in the materials.

4. Conclusions

In summary, we have investigated the influence of partial substitution of La by smaller ionic radii rare-earths elements in La$_{0.67}$Ca$_{0.33}$MnO$_3$ compounds. The Rietveld refinement of the X-ray data confirms that the RE (RE = Nd, Sm, and Gd) elements successfully substitute the La in the La$_{0.67}$Ca$_{0.33}$MnO$_3$ compound. The substitution of La by smaller radii ionic radii RE elements (La$_{0.67-x}$RE$_{x}$Sr$_{0.33}$) reduced the effective radii of A-site, (a$_r$), which alter the Mn–O bond length and Mn–O–Mn angles, but the Crystal structure of the compound remains unchanged. Our analysis of electrical and thermal transport data suggests that the mechanism of high-temperature transport is dominated by small polaron hopping, whereas the electron–magnon scattering plays the dominating role at low temperatures. The phenomenological percolation model could reproduce the resistivity data in the whole temperature range, suggesting the segregation of FM metallic clusters and PM insulating regions. Thermal conductivity is found to reduce with decreasing the ionic radii of dopant, indicating the destabilization of Jahn-Teller (J – T) distortion. Most importantly, the TCR and MR enhance significantly with rare-earth doping in the La$_{0.67}$Ca$_{0.33}$MnO$_3$ system.

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