Influence of Ce doping on electrical and thermal properties of La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ (0.0 $\leq$ $x$ $\leq$ 0.7) manganites

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The effect of Ce-doping on structural, magnetic, electrical and thermal transport properties in hole-doped manganites La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ (0.0 $\leq$ $x$ $\leq$ 0.7) is investigated. The structure of the compounds was found to be crystallized into orthorhombically distorted perovskite structure. $dc$ Susceptibility versus temperature curves reveal various magnetic transitions. For $x$ $\leq$ 0.3, ferromagnetic regions (FM) were identified and the magnetic transition temperature ($T_C$) was found to be decreasing systematically with increasing Ce concentration. The electrical resistivity $\rho(T)$ separates the well-define metal-semiconducting transition ($T_{MS}$) for low Ce doping concentrations (0.0 $\leq$ $x$ $\leq$ 0.3) consistent with magnetic transitions. For the samples with 0.4 $\leq$ $x$ $\leq$ 0.7, $\rho(T)$ curves display a semiconducting behavior in both the high temperature paramagnetic (PM) phase and low temperature FM or antiferromagnetic phase. The electron–phonon and electron–electron scattering processes govern the low temperature metallic behavior, whereas small polaron hopping model is found to be operative in PM phases for all samples. These results were broadly corroborated by thermal transport measurements for metallic samples ($x$ $\leq$ 0.3) in entire temperature range we investigated. The complicated temperature dependence of Seebeck coefficient ($S$) is an indication of electron–magnon scattering in the low temperature magnetic ordered regime. Specific heat measurements depict a broadened hump in the vicinity of $T_C$ indicating the existence of magnetic ordering and magnetic inhomogeneity in the samples. The observation of a significant difference between $\rho(T)$ and $S(T)$ activation energies and a positive slope in thermal conductivity $\kappa(T)$ implying that the conduction of charge carriers were dominated by small polaron in PM state of these manganites.

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1. Introduction

The perovskite manganites material R$_{1-x}$A$_x$MnO$_3$ ($R$ being trivalent rare earth ions) can be either hole doped or electron doped depending on whether $A$ is a divalent alkaline earth ion such as Ca, Ba, Sr, Pb, etc. [1–3], or tetravalent such as Ce, Sn, Te, etc. [4–15]. Both classes of these materials exhibit a rich phase diagram as a function of temperature, magnetic field and doping, and illustrate the metal–insulator transition as well as the phenomenon of colossal magnetoresistance (CMR). The physical properties such as electrical resistivity, magnetization, susceptibility, Seebeck coefficient, specific heat and thermal conductivity, etc., have been studied extensively in the framework of double exchange (DE) interaction for the hole doped manganites so far [3]. On the other hand, it has been recognized that the tetravalent cation doping drives the valence state of Mn$^{3+}$ in the parent compound into a mixed-valence state of Mn$^{3+}$ and Mn$^{4+}$, i.e., possible electron-doped systems with electronic configurations of the type: $t_{2g}$ $e_{g}^0$ and $t_{2g}$ $e_{g}^1$ [4], and it is possible to utilized such electron-doped systems as functional spintronics devices in the future. These studies on the electron doped systems demonstrated that the basic physics in terms of Hund’s rule coupling between $e_g$ electrons and $t_{2g}$ core electrons and the Jahn–Teller (JT) effect due to Mn$^{3+}$ JT ions can operate in the electron doped manganites as well [4–15].

In detailed, it is recognized that the study of A-site doping with divalent/tetravalent elements is vital to provide important clues to the mechanism of CMR. In particular, the tetravalent Ce enters at A-site would induce a metal–insulator (M–I) transition accompanied by the occurrence of ferromagnetic ordering with no observable thermal hysteresis at transition temperatures. Such a
finding implies that the phase transitions in these manganites can be regarded as a second-order phase transition with no latent heat at transition temperature [15]. Das and coworkers have prepared Ce doped polycrystalline La$_{1-x}$Ce$_x$MnO$_3$ ($0.0 \leq x \leq 0.6$) samples and found a metal–insulator transition at about 225 K [16]. The electrical resistivity $\rho(T)$ data reveals that the double peaks observed in the $\rho(T)$ data of ceramic samples are originated from the grain boundary effects. Moreover, it has been established that the charge conduction at higher temperature occurs by means of a thermally activated polaron hopping mechanism through electrical and thermopower analysis. In the Pr-doped La$_{0.9-x}$Pr$_x$Te$_{0.1}$MnO$_3$ ($x \geq 0.36$) manganites, the Curie temperature ($T_C$) is found to be decreased and the transition becomes broader with increasing Pr-doping concentration. However, for the samples with $x \leq 0.36$, the M-I transition is clearly observed [14].

Besides the Mn$^{3+}$/Mn$^{4+}$/Mn$^{4+}$ ratio, the average ionic radius of the A-site element $\langle r_A \rangle$, another substantial parameter that can also influence the DE mechanism [17–21]. The most important effect of decreasing $\langle r_A \rangle$ is to reduce the Mn–O–Mn bond angle, thereby reducing the matrix element that described electron hopping between Mn sites [20,21]. Moreover, for Pr$_{0.5-x}$Ce$_x$Mn$_{0.5}$O$_3$ doped manganites ($0.03 \leq x \leq 0.20$), the Ce substitution induces significant modifications in structural, magnetic, and transport properties due to the cation disorder and size effects [22]. Thus, A-site tetravalent cation-doping is expected to significantly affect the structural, magnetic, and transport properties in manganites, and a detailed investigation on the influence of simultaneous presence of hole and electron (Mn$^{3+}$/Mn$^{4+}$/Mn$^{4+}$) doping is desired. As mentioned above, manganese can have three valence states: Mn$^{4+}$, Mn$^{3+}$ and Mn$^{2+}$. In a divalent ion doped manganites system the manganese ion exists in trivalent and tetravalent states, but if the rare-earth ion is partially replaced by tetravalent ion the corresponding amount of manganese will be converted into a divalent state. With this notion in mind, we have examined a series of La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ samples, in which the average ionic radius of the A-site element $\langle r_A \rangle$ is systematically varied with varying Mn$^{3+}$/Mn$^{2+}$ (La$^{3+}$/Ca$^{2+}$) ratio while keeping the Mn$^{4+}$/Ca$^{2+}$ content fixed at 30% in this study.

It is revealed that the average ionic radius of the A-site element $\langle r_A \rangle$ has strongly affected the physical properties of parent hole doped La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ ($0.0 \leq x \leq 0.7$) manganites. In addition, the ferromagnetic regions (FM) were identified in $\chi$ susceptibility measurement and the magnetic transition temperature ($T_C$) was found to be decreasing systematically with increasing Ce concentration or decreasing $\langle r_A \rangle$ for $x \leq 0.3$. The electrical resistivity $\rho(T)$ separates the well-defined metal–semiconducting transition for low Ce doping concentrations ($0.0 \leq x \leq 0.3$) consistent with magnetic transitions. For the samples with $0.4 \leq x \leq 0.7$, $\rho(T)$ curves display the semiconducting behavior in both the high temperature paramagnetic (PM) phase and low temperature FM or antiferromagnetic (AFM) phase. The observed results are discussed in terms of electron–phonon, electron–electron and electron–magnon scattering processes in the metallic regions, while small polaron conduction mechanism is found to be operative in semiconducting regime in these manganites.

2. Experimental procedures

Polycrystalline samples of La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ ($0.0 \leq x \leq 0.7$) were prepared following a conventional solid-state reaction technique. Mixture of stoichiometric amount of La$_2$O$_3$, CeO$_2$, CaCO$_3$, and MnO$_2$ was calcined (at 900 °C) in air for 24 h with intermediate grindings, which were procured, from e-Merck and all the chemicals were of GR grade. After being palletized, the samples were sintered at 1000 °C for 24 h, and the pellets were finally annealed at 1000 °C in oxygen atmosphere [23]. The powder X-ray patterns were recorded using a Rigaku Diffractometer with Cu $K\alpha$ radiation. A scanning rate of 0.02 s$^{-1}$ was adopted and the data were taken at room temperature in the 20 range of 10–80°. It is observed that single-phase materials have been obtained in the entire range of doping under consideration, and are found to crystallize into orthorhombically distorted perovskite structure and is shown in Fig. 1. Magnetic properties were measured by a superconducting quantum interference device SQUID magnetometer (Quantum Design magnetic properties measurement system). Resistivity measurement was carried out by standard four probe method in a helium closed cycle refrigerator. The Seebeck coefficient and thermal conductivity measurements were carried out simultaneously from 10 to 350 K by using a direct heat pulse technique. Specific heat was measured from 70 to 350 K with a high-resolution ac calorimeter, using chopped light as heat source. Details of the electrical and thermal measurements techniques are described elsewhere [24].

3. Results and discussion

3.1. Magnetic properties

We have measured the temperature dependence of field-cooled (FC) and zero-field-cooled (ZFC) $\chi$ susceptibility for the La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ polycrystalline samples with $0.0 \leq x \leq 0.7$ and the results are shown in Figs. 2 and 3. The paramagnetic to ferromagnetic (PM–FM) transition temperature ($T_C$) were obtained from the minimum of the $d\chi/dT$ (inset of Fig. 2(a) refers to $x=0.0$ sample) and listed in Table 1. A strong hysteresis in $\chi$ susceptibility was observed, as indicated by the large bifurcation in the FC and ZFC curves. However, the $\chi$ susceptibility for $x=0.1$ and 0.2 samples shows a gradual drop at low temperatures (see Fig. 2(b) and (c)), indicating the occurrence of another magnetic transition to the AFM in these samples. The drop in magnetic moment could be due to the antiferromagnetic response from the rare earth element Ce or the short-range ordering of Mn$^{3+}$ and Mn$^{4+}$, which leads to the charge ordered AFM state [25]. It can be seen from the Table 1 that the $T_C$ decreases monotonically with increasing Ce-doping level. The reduction in $T_C$ is presumably ascribed to the presence of Mn$^{2+}$/Mn$^{3+}$/Mn$^{4+}$ ions and reduction in average ionic radius of
A-site element $\langle r_A \rangle$. The latter feature could readily increase the characteristic GdFeO$_3$-type distortion of the materials so as to decrease the Mn–O–Mn bond angle. As a consequence, double exchange interaction becomes weaker due to the narrowing the corresponding 3d bandwidth and the reduction the electron hopping between Mn sites [14].
For higher doped samples (0.4 ≤ x ≤ 0.7), which are in semi-conducting region, the dc susceptibility data infers PM–FM transition at much lower temperatures (see Fig. 3) due to the higher Ce ions concentration in these samples where Mn$^{3+}$ is, to the first approximations, replaced by Mn$^{2+}$ ions considerably. Besides, the measured γ is orders of magnitude smaller than that of the low-doping samples (0.0 ≤ x ≤ 0.3), indicating that the magnetic ordering herein is of different character from that in 0.0 ≤ x ≤ 0.3. Further considering the principally antiferromagnetic feature for samples of 0.4 ≤ x ≤ 0.7 observed upon zero-field cooling and the corresponding hysteresis upon field cooling (Fig. 3), it is possible that the magnetic ground state of these materials could be of the A-type ordering general for these manganites. Upon A-type ordering, the characteristic inter-plane antiferromagnetic coupling has been known to be susceptible by external fields, giving rise to hysteresis feature upon ZFC–FC history [26]. The different magnetic ground state also has a decisive influence on the electrical transport of these manganites, as we will discuss in the later sections.

### Table 1
Calculated parameters of dc susceptibility and electrical resistivity for La$_{0.7-}$.Ce$_x$.Ca$_{0.3}$MnO$_3$ (0.0 ≤ x ≤ 0.7) manganites.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>dc susceptibility</th>
<th>Electrical resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting parameters (Å)</td>
<td>$T_C$ (K)</td>
<td>$T_{MS}$ (K)</td>
</tr>
<tr>
<td>La$_0$.Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.205</td>
<td>250</td>
<td>255</td>
</tr>
<tr>
<td>La$_0$.Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.203</td>
<td>238</td>
<td>236</td>
</tr>
<tr>
<td>La$_0$.Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.201</td>
<td>220</td>
<td>222</td>
</tr>
<tr>
<td>La$_0$.Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.199</td>
<td>149</td>
<td>155</td>
</tr>
<tr>
<td>La$_0$.Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.197</td>
<td>47</td>
<td>–</td>
</tr>
<tr>
<td>La$_0$.Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.195</td>
<td>46</td>
<td>–</td>
</tr>
<tr>
<td>La$_0$.Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.193</td>
<td>41</td>
<td>–</td>
</tr>
<tr>
<td>Ce$<em>0$.Ca$</em>{0.3}$MnO$_3$ ($\langle \gamma \rangle$) = 1.191</td>
<td>42</td>
<td>–</td>
</tr>
</tbody>
</table>

#### 3.2. Electrical resistivity

Fig. 4 displays the temperature dependence of the electrical resistivity $\rho(T)$ of the La$_{0.7-}$.Ce$_x$.Ca$_{0.3}$MnO$_3$ polycrystalline samples with 0.0 ≤ x ≤ 0.7 in the temperature ranges from 0 to 400 K. The most noticeable feature of the resistivity curves is the metal–semiconducting (M–S) transition in the temperature range from 150 to 300 K for low doping concentrations (0.0 ≤ x ≤ 0.3). The M–S transition temperature ($T_{MS}$), determined from the maximum of $d\rho/dT$, is listed in Table 1 and found to be decreasing with decrease $\langle \gamma \rangle$ or increase in Ce content, consistent with corresponding PM–FM transition ($T_c$). It is clearly seen from Table 1 that the Curie temperatures $T_c$ determined from the magnetization measurements are consistently lower than those of the M–S transition temperatures $T_{MS}$ determined from the electrical resistivity measurements, i.e., the metal–insulator transitions take place in the paramagnetic phase. Such a behavior is commonly observed in the doped manganites system, and the discrepancy between different transition temperatures is ascribed to the coexistence and competition between Mn$^{3+}$–Mn$^{4+}$ double exchange and Mn$^{2+}$–Mn$^{3+}$ ferromagnetic superexchange interaction. On the other hand, higher doping samples (0.4 ≤ x ≤ 0.7) showing semiconducting-like behavior throughout the temperature range we measured (see inset of Fig. 4). It is noteworthy to point out here that we do not observe double peak in electrical resistivity data as reported for Ce doped manganites in the literature [5,6,16], reflecting the high quality of our samples.

For metallic samples (0.0 ≤ x ≤ 0.3), the samples with higher Ce concentration show a higher resistivity and this is attributed to the fact that the Mn$^{3+}$ content is reduced by the addition of Ce ions. However, such a trend is found to be opposite in semiconducting samples (0.4 ≤ x ≤ 0.7). It is well known that observed M–S transition in manganites is governed by two competing effects. The DE magnetic interaction, which can increases the electron kinetic energy and hence delocalizes the charge carriers [3]. On the other hand, the localization of the carriers in a local lattice distortion takes place due to strong J–T coupling [3]. The interplay between charge localization and distortion of the octahedral also occurs when the metallic phase is being approached by varying other parameters, such as A-site cation ionic radius. The underlying idea is that a M–S transition occurs if the octahedral are forced to be undistorted and the Mn–O–Mn angle tends to 180°. In other words, a sufficient reduction of the free volume around the A-site is obtained. This can be achieved either by contracting the cage of the MnO$_6$ octahedral or by increasing the average dimension of the A-site [17–20] as in the present case where the internal pressure generated by the interpolated by A-site cation (see Table 1).

Based on the above discussion and strong correlation effect present in manganites [3], the electrical resistivity in metallic
region ($T < T_{R0}$) of La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ (0.0 ≤ x ≤ 0.3) is theoretically analyzed. We have considered the scattering of charge carriers with high-energy optical and acoustic phonons in order to estimate the temperature-dependent electrical resistivity. The other possibility for the change in carrier density arises due to the presence of electron–electron correlation in the metallic system. The electron–electron contribution usually follows $T^2$ behavior in a disordered system. We have thus fitted the metallic resistivity following:

$$\rho(T) = \rho_0 + BT^2 + \rho_{e-ph}(T)$$  \hspace{1cm} (1)

here the first term is the residual resistivity and other two terms in Eq. (1) are related to the electron–electron and electron–phonon contribution, respectively [27–29]. Here, $B$ is a constant, which provides the strength of electron–electron scattering, whose deduced values are found to be decreasing with increasing Ce concentration and are listed in Table 1.

The electron–phonon contribution, following the Bloch–Gruneisen (BG) method allows us to estimate the independent contributions of acoustic and optical phonons. The temperature dependent part of the resistivity within the harmonic approximation results [29]

$$\rho_{e-ph}(T) \approx \left( \frac{3}{\hbar e^2 v_s^2} \right) \frac{k_B T}{M \omega_c} \int_0^{2\pi} \left| F(q) \right|^2 \frac{x^q dq}{\sinh(x)}$$  \hspace{1cm} (2)

with $x = \hbar \omega / k_B T$. In the above equation, $F(q)$ is the Fourier transform of the potential associated with one lattice site, $v_s$ and $v_c$ are the Fermi velocity and sound velocity, respectively. In terms of Debye type of acoustic phonon ($\Theta_a$) contribution, the Eq. (2) yields the Bloch–Gruneisen function of temperature dependence electrical resistivity

$$\rho_{ac}(T) = 4A_{ac} T / \Theta_a \int_0^{\Theta_a / T} \frac{x^2}{\sinh(x)} dx,$$  \hspace{1cm} (3)

where $A_{ac}$ is a constant of proportionality defined as

$$A_{ac} \approx \frac{3\pi^2 e^2 k_B}{k_F^2 v_s^2 L \hbar v_F M}$$  \hspace{1cm} (4)

On the other hand, in case of the Einstein type of optical phonon spectrum ($\Theta_E$), $\rho_{op}(T)$ may be described as follows:

$$\rho_{op}(T) = \frac{A_{op} \Theta_E^3}{(e^{\xi/\Theta_E} - 1)(1 - e^{-\xi/T})},$$  \hspace{1cm} (5)

here the constant $A_{op}$ is defined analogous to Eq. (4). Thus, the phonon electrical resistivity can be conveniently modeled by combining both terms arising from acoustic and optical phonons as

$$\rho_{e-ph}(T) = \rho_{ac}(T) + \rho_{op}(T).$$  \hspace{1cm} (6)

Fig. 5, thus illustrates the results of temperature dependence of electrical resistivity in the metallic region where the scattering of carriers via electron–electron and electron–phonon have been accounted in Eq. (1). The values of coefficients ($A_{ac}$ and $A_{op}$), obtained for different Ce concentration resulting from electron–phonon temperature-dependent contribution of electrical resistivity, are listed in Table 1. The obtained values of coefficients $A_{ac}$ and $A_{op}$ are comparable with the earlier results on manganites [23]. Here, we have used the values of $\Theta_D$ and $\Theta_E$ from our specific heat data (see Table 2). For the sake of simplicity, a single (longitudinal and transverse) optical phonon mode has been considered with a flat dispersion relation. The electron–phonon interaction constants ($A_{ac}$ and $A_{op}$) are found to be systematically increasing with increasing $x$. Further, $A_{op}$ is larger than $A_{ac}$, such a trend is interpreted as a direct consequence of the enhancement of electrical resistivity due to the high-energy optical phonon

is attributed to the significant optical phonon hardening effect on carrier transport. The existence of quadratic temperature dependence of resistivity over a wide temperature interval suggested that the electron–electron scattering is also significant in determining the electrical resistivity in manganites.

Furthermore, we have analyzed the high temperature electrical resistivity data in the PM region for both metallic (0.0 ≤ x ≤ 0.3) and as well as semiconducting (0.4 ≤ x ≤ 0.7) samples in the framework of adiabatic small polaron conduction (SPC) model [30]. In the polaronic conduction, the most rapid motion of a small polaron occurs when the carrier hops each time the configuration of vibrating atoms in an adjacent site coincides with that in the occupied site. Henceforth, the charge carrier motion within the adiabatic regime is faster than the lattice vibrations and the resistivity for SPC follows [30].

$$\rho = \frac{k_B T}{n(1-x)e^2 D} \exp \left( \frac{E_p}{k_B T} \right),$$  \hspace{1cm} (7)

where $n$ is the charge carrier density, $x$ is the doping fraction, $e$ is the electronic charge, $E_p$ is the polaron formation energy and $k_B$ is the Boltzmann constant. Here, $D$ is the polaron diffusion constant ($D = \alpha^2 v/6$ for a typical cubic coordination, where $\alpha$ is the lattice constant and $v$ is the characteristic frequency of the longitudinal optical phonon that carries the polaron through the lattice). In Fig. 6 we have plotted the electrical resistivity data with Eq. (7) and it is found to be following over most of the temperature, supporting the idea that the charge conduction takes place via polaron hopping. The polaron formation energy obtained from the fitting is summarized in Table 1 for (0.0 ≤ x ≤ 0.7). It is noticed that $E_p$ is increasing with $x$ in both metallic (0.0 ≤ x ≤ 0.3) and semiconducting (0.4 ≤ x ≤ 0.7) samples, which is a result of reduction of favorable sites available for polaron hopping due to the reduction of Mn$^{4+}$ ions. Although we have provided a simple explanation of these effects, there is a clear need for good theoretical understanding of the resistivity behavior, in view of the fact that formation of small polarons may be of magnetic origin in manganites.
Among various transport properties, Seebeck coefficient is a sensitive tool for understanding the scattering mechanisms that dominate the electronic conduction. Similar to high temperature superconductors, the Seebeck coefficient of manganites shows strong temperature dependence and the sign of Seebeck coefficient could yield valuable information of the effect of substitution by the divalent/tetravalent cation that determines the transport in the system [31–34]. The variation of Seebeck coefficient could yield valuable information of the effect of substitution by the divalent/tetravalent cation that determines the thermoelectric transport in this temperature range, i.e., below PM state.

3.3. Seebeck coefficient

Among various transport properties, Seebeck coefficient is a sensitive tool for understanding the scattering mechanisms that dominate the electronic conduction. Similar to high temperature superconductors, the Seebeck coefficient of manganites shows strong temperature dependence and the sign of Seebeck coefficient could yield valuable information of the effect of substitution by the divalent/tetravalent cation that determines the carrier density in the system [31–34]. The variation of Seebeck coefficient with temperature is shown in Figs. 7 and 8 for $La_{0.7-x}Ce_xCa_{0.3}MnO_3$ polycrystalline metallic ($0.0 \leq x \leq 0.3$) and semiconducting ($0.4 \leq x \leq 0.7$) samples, respectively. It is seen in the figures that the Seebeck coefficient of $La_{0.7-x}Ce_xCa_{0.3}MnO_3$ shows a rather complicated temperature dependent corresponding to different magnetic and conducting states. For metallic samples, a step like behavior has been shown by $S(T)$ data in the vicinity of electrical and magnetic transitions. Initially, the absolute value of $S$ increases with increasing temperature up to 20 K and exhibits a small phonon drag maximum. In the low temperature regime ($T < 20$ K), the $S(T)$ shows linear temperature dependence. This indicates that the Seebeck coefficients are to follow $S \propto T$ (i.e., bare metallic diffusion Seebeck coefficient). As temperature increases above 20 K, $S(T)$ deviates from the linear temperature dependence and developed a phonon-drag peak below 50 K. On increasing temperature further, a broad maximum in intermediate temperature regime appears. A likely explanation of the variation of $S$ with $T$ in intermediate temperature regime is originated from the magnon. In general, the $S(T)$ of manganites in the intermediate temperature regime could be analyzed by the following equation [31–34]:

$$S(T) = S_0 + S_{3/2}T^{3/2} + S_4T^4,$$  \hspace{1cm} (8)

where $S_0$ accounts for the problem of truncating the low temperature data, which has no physical origin [31–34]. The second term of the equation represents the electron–magnon scattering processes (magnon drag), and the last term is related to the spin wave fluctuations in the magnetically ordered state. In FM and AFM states, electrons are scattered by spin waves. Analogous to the phonon drag effect, the electron–magnon interactions produce magnon drag effect. As the magnon drag effect is approximately proportional to the magnon specific heat, one expects a $T^{3/2}$ contribution in $S$ at low temperatures. We have fitted $x = 0.0$ data as one of the representative sample in metallic phase and the result is shown in Fig. 7 by thick continuous line. The fitting parameters are $S_0 = -1.5 \mu V K^{-1}$, $S_{3/2} = 2.33 \times 10^{-2} \mu V K^{-3/2}$ and $S_4 = -3.0 \times 10^{-9} \mu V K^{-5}$, consistent with the earlier reported data of manganites [31–34]. Further, it is noted that the parameter $S_{3/2}$ is five orders of magnitude larger than $S_0$, implying the second term (electron–magnon scattering) in Eq. (8) dominates the thermoelectric transport in this temperature range, i.e., below PM state.
On the other hand, the magnitude of $S$ is found to increase with increasing temperature throughout the temperature range for semiconducting ($0.4 \leq x \leq 0.6$) samples. The $x=0.7$ sample (Ce$_{0.7}$Ca$_{0.3}$MnO$_3$) has shown somewhat different temperature variation in comparison to other semiconducting samples. Such a dramatic change in $S$ is presumably due to the complete substitution of La$^{3+}$ ion by Ce$^{4+}$ that severely changes the ratio of amount of Mn$^{3+}$/Mn$^{4+}$, and hence greatly affects the double exchange and conduction process. Based on the electrical resistivity and $S(T)$ data, we have explored various mechanisms operating in the semiconducting region for all the samples. It is worth mentioning that the effect of J-T distortion in manganites generally results in the possibility of strong electron-phonon coupling and hence the formation of polarons [3]. Therefore, charge carriers in the semiconducting region are not itinerant and the transport properties are governed by thermally activated carriers (polarons). In the semiconducting region, if polaronic conduction dominates the carrier transport, $S(T)$ should follow the relation (SPC model) [30]:

$$S = \frac{k_B}{e} \left[ \frac{E_S}{k_BT} + \alpha \right]$$

(9)

where $k_B$ is the Boltzmann constant, $e$ is the electronic charge, $E_S$ is the activation energy, and $\alpha$ is a sample-dependent constant which is associated with the spin and the mixing entropy. Here, $\alpha < 1$ infers the conduction is the small polaron hopping, whereas $\alpha > 2$ represents the existence of a large polaron [30]. Therefore, at least two conditions should be fulfilled for conduction due to small polaron hopping, i.e., the value of $\alpha < 1$ at the same time $E_S < E_p$, where $E_p$ is the polaron formation energy obtained from the fitting of $\rho(T)$ data above $T_M$ following the SPC model. The fitting is illustrated in Figs. 7 and 8 (solid lines) and the fitting parameters $\alpha$ and $E_S$ are listed in Table 2 for all the samples (except for $x=0.7$). Deduced values of $\alpha$ is found to be less than unity and the magnitude of $E_S$ is much smaller than that of $E_p$ (from Table 1), confirming that the carrier conduction is through the hopping of small polarons in the semiconducting region.

Fig. 7. Variation of the Seebeck coefficient as a function of temperature for La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ ($x=0.0-0.3$) metallic manganites. The solid lines represent the fitting of data according to the Eq. (8) for $x=0.0$ in metallic region and to the SPC model using Eq. (9) for $x=0.0-0.3$ in semiconducting region.

Fig. 8. Showing the Seebeck coefficient and fitted curve following SPH model (solid line) as a function of temperature for La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ ($x=0.4-0.6$) manganites. The inset represents the temperature dependent behavior of the Seebeck coefficient for $x=0.7$ sample.

Fig. 9. The heat capacity as a function of temperature for La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ for $x=0.0$ sample. The solid line represents the estimated background. The inset shows the excess heat capacity $\Delta C_p$ for $x=0.0-0.3$.

3.4. Specific heat

The $T$-dependent specific heat ($C_p$ versus $T$) of La$_{0.7-x}$Ce$_x$Ca$_{0.3}$MnO$_3$ for metallic samples ($0.0 \leq x \leq 0.3$) is illustrated in Figs. 9 and 10. Each curve in Fig. 10 is offset by 10[J/mol K] for clarity. Note that $ac$ technique does not give the absolute value of specific heat without detailed knowledge of the power absorbed from the light pulse. The absolute value of the specific heat above 130 K is determined by measuring a powder sample ($\sim 200$ mg) using a differential scanning calorimetry (DSC). The $ac$ results
were corrected for their addendum heat capacities (GE varnish and thermocouple wire) and normalized to the DSC data at 200 K. It is seen that only the La_{0.7}Ce_{0.3}MnO_3 (x=0) sample shows sharp peak, consistent with earlier reported specific heat in Ce substituted manganites [35,36]. However, other samples (0.1 ≤ x ≤ 0.3) have much broader peak in C_p(T) curves corresponding to these samples. The observed anomaly in C_p(T) is in the vicinity of magnetic and electrical transitions, presumably associated with the magnetic ordering in these samples. We found that the observed peak in C_p(T) shifted towards lower temperatures and becomes progressively broader with increasing Ce-doping and finally smearing at higher doping (x=0.3). The observed broadening in the C_p(T) anomaly with Ce substitution implies the increase in magnetic inhomogeneity, caused by the weakening of the double-exchange mechanism with Ce ion that hinders the transfer of electrons between Mn^{3+}/Mn^{4+} pairs. It is instructive to mention that the broadening of anomaly in C_p(T) is commonly seen for oxides materials containing multiple chemical constituents.

At room temperature the value of heat capacity is about 124 J/mol K for all samples, in well accordance with the previous high temperature specific heat measurements performed on this class of materials for a system made up of molecules containing five atoms [35–40]. Following Dulong–Petit’s law, the limiting specific heat h_{CP}(300 K), the observed C_p(300 K), which is about 99.4% of the theoretically calculated value, indicating reliable C_p data and good quality of the samples. In principle, the specific heat measurements could provide information about both lattice and magnetic excitations. At high temperatures, the excitations from the lattice vibrations are expected to dominate and decrease as the temperature decreases. Indeed, the above comparison of C_p(300 K) between the observed and theoretical (lattice vibrational) value signifies that the bulk of the contribution essentially comes from vibrational heat capacity. One can obtain the magnetic contribution for the specific heat by subtracting the lattice part from the experimental data. The solid curves in Figs. 9 and 10 represent the fitting of the thermal backgrounds, in the interval from 70 K to 350 K, using the Einstein model given by [41]:

\[
C_{\text{Einstein}} = 3\pi^2 \sum_i \frac{k}{h} \frac{\omega_i^2 e^{-\frac{\hbar \omega_i}{kT}}}{(e^{\frac{\hbar \omega_i}{kT}} - 1)^2},
\]

here \(\omega_i = \frac{h \nu_i}{kT}\). Three optical phonons \(i=1, 2, 3\) having Einstein frequencies \(\nu_i\) and relative occupations \(a_i\) were used. The Einstein model for the specific heat considers the oscillation frequency \(\nu_i\) independent of the wave vector which is a valid approximation for the optical part of the spectrum. The best fits of the data given the three Einstein modes with the estimated Einstein temperatures \(\Theta_E = h \nu_i/k_B\) are listed in Table 2.

We also have tried to estimate specific heat due to collective low frequency oscillations of phonons in a framework of a Debye model. We found that the data could not be fitted using a single Debye function over the entire temperature range we studied (not shown here). The estimated values of \(\Theta_E\) and \(\Theta_D\) extracted from the high from temperature specific heat data for these samples are also listed in Table 2 and are in agreement with previously published values of \(\Theta_E\) and \(\Theta_D\) for Ca doped manganites materials [37,39]. In the inset of Fig. 9 we show the specific-heat jumps \(\Delta C_p\) near the transitions in La_{0.7−x}Ce_{x}Ca_{0.3}MnO_3 samples (0.0 ≤ x ≤ 0.3) by subtracting the lattice background estimated from the Einstein model. It is clearly seen a suppression of \(\Delta C_p\) with increase in Ce-content, confirming the increase in magnetic inhomogeneity with Ce-doping [28]. The source of this magnetic inhomogeneity could be the polycrystalline nature of the samples and also the possible occurrence of antiferromagnetic interaction arising with Ce doping and thus weakens the double-exchange mechanism and promotes the superexchange mechanism that is antiferromagnetic in nature. The enhancement of magnetic inhomogeneity with Ce doping also results in a reduction of spin polarization that is reflected in the Seebeck coefficient measurements where a decrease in the electron to hole-like transition temperature is observed.

3.5. Thermal conductivity

In order to further elucidate other distinguishing features of these materials, we have also measured the temperature dependent

Fig. 10. The heat capacity as a function of temperature for La_{0.7−x}Ce_{x}Ca_{0.3}MnO_3 for x=0.1–0.3 samples. The solid line represents the estimated backgrounds.

Fig. 11. Variation of thermal conductivity as a function of temperature for La_{0.7−x}Ce_{x}Ca_{0.3}MnO_3 (x=0.0–0.3) along with fitting (solid lines) to the Eq. (11) in the high temperature range. The inset shows the thermal conductivity as a function of temperature for x=0.4–0.7 samples.
thermal conductivity $\kappa(T)$ between 10 and 300 K (shown in Fig. 11). Since the results of thermal conductivity provide valuable information about various scattering processes of thermal carriers, the present data would offer an opportunity to probe the interplay between the lattice and charge degrees of freedom in these manganites. It should be mentioned here that the measured values of $\kappa(300\text{ K})$ are rather small and comparable to those of glassy materials [42]. For typical non-crystalline materials (bad metals), the magnitude of $\kappa(300\text{ K})$ lies in the range of 5–65 mW/cm K. For a crystalline solid, such a low value of thermal conductivity can be thought to originate from various disorders present in the lattice, such as random, noncentral distortions of the lattice, etc., resulting in high degree of disorder. Comparing thermal conductivity data of various perovskites manganites [43,44], such a scenario may be attributed to the vibronic interactions of Mn$^{3+}$ (Jahn–Teller) ions, which critically limit the mean free path of phonons. It can be seen from the Fig. 11 that the thermal conductivity data also depicts substantial differences between metallic and semiconducting compositions. At low temperatures, $\kappa$ increases with temperature and a maximum appears around 40 K for the samples having low temperature metallic phase ($0.0 \leq x \leq 0.3$). Such an observation is a typical feature for the reduction of thermal scattering in solids at low temperatures. With further increase in temperature, $\kappa$ decreases with temperature due to the enhanced phonon–phonon scattering (umklapp processes) [34]. We emphasized here that the total thermal conductivity is mainly associated with the lattice phonons rather than the charge carriers, due to the high electrical resistivity of these perovskites. For instant, the estimated electronic thermal conductivity ($\kappa_e$) contribution from the Wiedemann–Franz law [42] is of about 0.90 mW/cm K for the most conducting sample ($x=0.0$) at room temperature, much smaller as compared to the total thermal conductivity. Consequently, the predominant contribution to the measured $\kappa$ comes from phonon thermal conductivity ($\kappa_{ph}$) with a negligibly small contribution of $\kappa_e$.

It is found that the low temperature hump disappeared for those samples which are having low temperature semiconducting phase. In fact, the observed low temperature hump becomes considerably broadened as we approach towards semiconducting phase. Further, $\kappa$ is found to be decreasing with increasing temperatures till the occurrence of the transition for metallic samples ($x \leq 0.3$). However, it is found to be nearly saturating above 50 K for semiconducting samples ($x > 0.3$). On the other hand, in the case of metallic samples, the simultaneous magnetic ($T_C$) and M–S ($T_{MS}$) transitions are accompanied by a sharp increase of $\kappa$ and the observed thermal conductivity displays the behavior of an amorphous solid, i.e., $d\kappa/dT > 0$, as seen from Fig. 11. Such observations are similar to the case of hole-doped manganites [43]. Usually the high temperature thermal conductivity of the crystalline insulators is mostly a decreasing function of temperature and cannot be attributed to high temperature electron or phonon processes. Such an unusual behavior of $\kappa(T)$ above $T_C$ may be attributed to the local anharmonic lattice distortions associated with small polaron [45], consistent with our electrical resistivity and the Seebeck coefficient results. Moreover, to get quantitative view above $T_C$, $\kappa(T)$ can be expressed as the following:

$$\kappa(T) = \kappa_0 \exp \left( \frac{T}{\tau} \right). \quad (11)$$

here, $\kappa_0$ and $\tau$ are the fitting parameters and listed in Table 2, comparable with previously reported results on manganites [45]. In Fig. 11, the solid line represents the fit with Eq. (11) in the high temperature range for La$_{0.7-x}$Ce$_x$Co$_{0.3}$Mn$_{0.7}$O$_3$ ($0 \leq x \leq 0.3$) samples. $\tau$ is found to be increasing with increasing Ce concentration, a direct consequences of the degree of local anharmonic lattice distortions associated with small polaron, consistent with the other transport properties as observed in the PM phases of these samples.

4. Conclusions

The effect of Ce-doping on structural, magnetic, electrical and thermal transport properties in hole-doped manganites La$_{0.7-x}$Ce$_x$Co$_{0.3}$Mn$_{0.7}$O$_3$ ($0 \leq x \leq 0.7$) is systematically investigated. In dc susceptibility measurements, ferromagnetic regions (FM) were identified and the magnetic transition temperature ($T_C$) was found to be decreasing systematically with increasing Ce concentration ($0.0 \leq x \leq 0.3$). For the samples with $0.4 \leq x \leq 0.7$, $\rho(T)$ curves display the semiconducting behavior in both the high temperature paramagnetic (PM) phase and low temperature FM or antiferromagnetic (AFM) phase. These results were broadly corroborated by thermal transport measurements, namely, the Seebeck coefficient and thermal conductivity in entire temperature range we investigated for metallic samples ($x \leq 0.3$). The observed results are discussed in terms of electron–phonon, electron–electron and electron–magnon scattering processes in the metallic regions, while small polaron conduction mechanism is found to be operative in semiconducting regime in these manganites.

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