Structural, electrical and thermal studies of Nb-doped Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ (0 ≤ x ≤ 0.05) manganites

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**Abstract**

X-ray diffraction (XRD), electrical resistivity (ρ) and thermal measurements of thermopower (S), thermal conductivity (κ), and specific heat (C$_T$) of Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ (0 ≤ x ≤ 0.05) manganite samples are reported here. XRD and electrical resistivity measurements have been carried out up to 5% Nb-doping whereas thermal measurements are limited up to 3% Nb-doping as higher doped sample exhibits a large value of electrical resistivity. With Nb-doping the lattice volume increases, which indicates the occupancy of Mn$^{4+}$ sites by Nb$^{5+}$ and eventually results in generating more Mn$^{3+}$ Jahn Teller active (JT) ions. Nb doping also reflects its repercussion in the ρ(T) behavior where the insulator-metal transition temperature of the pristine Pr$_{0.7}$Sr$_{0.3}$MnO$_3$ shifts to lower temperatures with increasing doping content. Based on the comparison of electrical resistivity and thermopower data, we establish that the strength of electron–phonon coupling increases with increasing Nb content. Thermal conductivity behavior κ(T) has been viewed in terms of the scattering of phonons by spin fluctuations and such a scenario has been corroborated with the specific heat data.

**1. Introduction**

Perovskite manganites (ABO$_3$, A = trivalent rare-earth ion or divalent alkali earth-ion and B = trivalent transition metal ion, generally a manganese ion) have been the subject of intense research during the last two decades because of the observation of the colossal magnetoresistance (CMR) effect and their potential for devices [1]. During the 1950s, when these materials were specially studied for their electrical and magnetic behavior, the double-exchange mechanism was proposed by Zener [2] to understand the conduction mechanism. Later on, it was found that electron–phonon coupling should also be taken into account to explain the insulator–metal (I–M) transition and the magnetoresistance behavior [1]. Their charge, spin and lattice degrees of freedom have also been reported to be intercoupled. However, despite intense research efforts a comprehensive understanding of the conduction mechanism and the observation of the CMR effect at lower magnetic fields are still elusive. The two ways to understand these issues are, either we dope some elements at the rare-earth site that indirectly modify the conduction mechanism taking place at the Mn-site, or we can directly tailor it by doping at the Mn-site. However, doping at the Mn-site has proven more effective in manipulating the conduction process. Recently, to explore the effect of doping, the focus has shifted towards the doping of higher valent ions at the Mn-site [3–13]. Liu et al. [3] reported the effect of Ti$^{4+}$ doping in La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) manganite and observed that Ti$^{4+}$ doping converted the paramagnetic–ferromagnetic (PM–FM) transition ($T_C$) into a paramagnetic-spin glass and the I–M transition shifted to lower temperatures with an increase in electrical resistivity. With higher Ti$^{4+}$ ion content the samples exhibited insulating behavior in the whole temperature range of measurement. Such behavior was attributed to the strong localization of holes with doping. Sridharan et al. [4] studied the transport properties of Fe$^{3+}$, Zr$^{4+}$ and Hf$^{4+}$ ions doped LCMO system and noticed that Zr$^{4+}$ and Hf$^{4+}$ suppressed the I–M transition more predominantly than the Fe$^{3+}$ ion due to the closed shell configuration of the former ions, which effectively blocked the double-exchange mechanism. Troyanchuk et al. [5] studied the magnetic interactions in Nb$^{5+}$-doped La$_{0.7}$Sr$_{0.3}$MnO$_3$ manganite and concluded that Mn$^{3+}$ ion rich samples La$_{0.7}$Sr$_{0.3}$ (Mn$_{0.85}$Nb$_{0.15}$)O$_3$
were ferromagnetic and showed a large magneto-resistance below $T_c$ due to the Mn\(^{3+}\)–O–Mn\(^{3+}\) exchange interaction being ferromagnetic in the orbitally disordered manganese. These samples were specially prepared to avoid the presence of Mn\(^{4+}\) ions. Sudyoadusk et al. [6] reported that the charge ordering transition temperature is suppressed in Sr\(^{2+}\) doped La\(_{0.9}\)Ca\(_{0.1}\)Mn\(_2\)O\(_3\) samples. V\(^{4+}\) doping introduced two transitions in the electrical resistivity, magnetization and specific heat of La\(_{0.9}\)Ca\(_{0.1}\)Mn\(_2\)O\(_3\), which was attributed to the phase-separation phenomenon [7]. Similar suppression of magnetic transition temperature and two peak resistivity behavior along with a low temperature resistivity minimum was also reported in Sr\(^{2+}\) doped LCMO system [8]. Substitution of V\(^{4+}\) ion doping was found to enhance the grain growth as well as the low field magneto-resistance [9, 10]. Recently, thermal properties of higher valent (such as Ru\(^{5+}\) and Gd\(^{5+}\)) doped manganese [11–15] have been studied, and based on these reports it can be concluded that thermal measurements such as thermopower (S), thermal conductivity (κ), and specific heat (C) may provide useful information regarding various conduction mechanisms operating at different temperatures. Small polarons, electron–magnon and electron–phonon interaction, phonon–photon scattering are some of the most important factors in such materials [16–19].

To understand such aspects, manganites with orthorhombic symmetry seem to be more preferable over rhombohedral ones because the former allows three independent Mn–O bond lengths to support the Jahn–Teller (JT) distortion, which leads to the formation of correlated JT polarons in the insulating paramagnetic regions. On the other hand, the lattice symmetry produces uniform Mn–O bond lengths and prevents coherent JT distortions of the Mn\(^{3+}\)O\(_6\) octahedra. In the thermal studies of Ruben et al. [14] and La\(_{2}\)Ba\(_{1/3}\)Sr\(_{2/3}\)Mn\(_2\)O\(_3\) (LBMO) [15] manganites it is observed that LBMO generally possesses a rhombohedral or cubic structure and its I–M transition (~340 K) is far above the room temperature (RT), whereas, the I–M transition of PIBM (~194 K) is far below RT even though it has orthorhombic structure. Moreover, these two manganite systems offer stronger grain boundary effects due to the large cationic size mismatch. Here in, we report the structural, electrical and thermal measurements on the Nb\(^{5+}\) ion-doped Nb\(_2\)O\(_5\) doped Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) (PSMO) system in which we have noticed the I–M transition around 280 K and the absence of grain boundary effects arising from the cationic mismatch in this system. The reason for choosing Nb\(^{5+}\) is that it has the inert shell electronic configuration of Kr and is not expected to produce any extra magnetic coupling, but it will modify the Mn\(^{3+}/\)Mn\(^{4+}\) ratio. The change in the Mn\(^{3+}/\)Mn\(^{4+}\) ratio would lead to some modifications and it would be worthwhile to examine how it affects the conduction process in the pristine PSMO system.

### 2. Experimental

Samples of the Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) (0 ≤ x ≤ 0.05) series were prepared by a conventional solid state reaction method. Materials with stoichiometric ratios of Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_2\)O\(_3\), Mn\(_2\)O\(_3\), and Nb\(_2\)O\(_5\) (all with 99.9% purity) were mixed in an agate-mortar to obtain a homogeneous mixture. These mixtures were calcined at 1250 °C for 12 h, pressed into pellets and sintered in air at 1400 °C for 24 h. The sintered pellets were annealed at 1100 °C in an oxygen atmosphere for 12 h followed by slow cooling (~2 °C/min) to room temperature. XRD patterns of the synthesized samples were recorded on a Rigaku Miniflex II machine with Cu K\(_\alpha\) radiation (1.54 Å). Electrical resistivity as a function of temperature was measured by the conventional four-probe method. Thermal and transport measurements have been limited up to 3% Nb-doping, as samples with higher doping showed large electrical resistivity. Details of the thermal measurements have been reported elsewhere [see 11, 15] and references therein.

### Table 1

<table>
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<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å(^3))</th>
<th>ρ(_\text{RT})</th>
<th>ρ(_\text{at}) T(_p)</th>
<th>χ(_0)</th>
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<td>3.51</td>
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### 3. Results and discussions

**Fig. 1** shows the X-ray diffraction patterns of the Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) (0 ≤ x ≤ 0.05) series. These samples exhibit a single-phase nature with an orthorhombic structure and a Pbnm space group. The Hume–Rothery criteria of solid solution formation viz. ionic size compatibility, coordination number, valence state and electronegativity [20] led us to believe that Nb-ions occupy the Mn-site and not the Pr/Sr. It is also observed from the inset of Fig. 1 that the main diffraction peak at ~32.76° shifts systematically to lower 2θ values with Nb doping, implying an increase in the unit cell volume. This could be possible only if Nb\(^{5+}\)-ion substitutes the smaller Mn\(^{4+}\)-ion instead of the Mn\(^{3+}\)-ion, which has compatible ionic size to that of Nb\(^{5+}\) [21]. Based on the Rietveld fitting of the XRD patterns, we calculated the lattice parameters, which corroborate the increase in unit cell volume with Nb doping (Table 1). Also, the lattice parameters of the pristine sample PSMO match very well with an earlier published report [22].

**Fig. 2** depicts the variation of electrical resistivity with temperature for the Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) (0 ≤ x ≤ 0.05) series. A peak in the resistivity at T\(_p\) ~ 280 K is observed for the pristine PSMO sample. With increasing Nb-doping (at the Mn-site), T\(_p\) shifts to lower temperatures along with an increase in the electrical resistivity viz. T\(_p\) goes down to 248 K, 163 K and 110 K with 1%, 3% and 5% Nb content respectively. This result can be understood on the basis of charge neutrality in the Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) system. With an increase in Nb\(^{5+}\) doping, the average valency at Mn-site shifts towards +3 by the following relation Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) → Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) + x Nb\(^{5+}\)O\(_4\). Therefore, with increase in Nb-concentration, more Mn\(^{3+}\) JT active ions are produced. This would lead to an enhancement of the super-exchange interaction in the Mn\(^{3+}\)O\(_2\)–Nb\(^{5+}\)O\(_3\) network and simultaneously suppress the double-exchange mechanism. To further observe the effect on activation energy due to a change in the Mn\(^{3+}\)/Mn\(^{4+}\) ratio with Nb-doping, we fitted the high temperature insulating region by Holstein’s small polaron hopping model [16]

$$\rho = \rho_0 \exp \left( \frac{E_p}{k_BT} \right)$$

where $\rho_0$ is a constant, $E_p$ is the polaron activation energy, and $k_B$ is the Boltzmann constant. The calculated activation energy using Eq. (1) for all the samples is listed in Table 2. The value of activation energy is found to increase with Nb doping. This may be due to the fact that besides Mn\(^{3+}\)O\(_2\)–Mn\(^{4+}\), there could be the formation of another network, e.g. Mn\(^{3+}\)O\(_2\)–Nb\(^{5+}\). Since Nb\(^{5+}\) has a closed shell structure of Kr, it is not expected to participate in any conduction process and will only lead to the localization of the carriers, and consequently an enhancement of the electrical resistivity in the doped samples.

**Fig. 3** shows the variation of thermopower (S) with temperature for the Pr\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1−x}\)Nb\(_x\)O\(_3\) (0 ≤ x ≤ 0.03) samples. The magnitude of S for the pristine PSMO sample at 300 K is ~10 μV/K, reminiscent of the insulating behavior. With decreasing temperature, S shows a transition that corresponds to the I–M transition at T\(_p\) in the electrical resistivity. Below the transition, S drops sharply and exhibits a crossover from negative to positive values, indicative of
Fig. 1. Rietveld fitted XRD patterns of Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ ($x = 0.0, 0.01, 0.03$ and $0.05$) samples. Inset shows the main peak shift with doping.

<table>
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<th>$T_F$ (K)</th>
<th>$E_p$ (meV)</th>
<th>$E_f$ (meV)</th>
<th>$E_S$ (meV)</th>
<th>$\alpha$</th>
<th>$\theta_B$ (K)</th>
<th>$\nu_{ph} \times 10^{12}$ (Hz)</th>
<th>$\gamma$</th>
<th>$\Delta S$ (J/mol K)</th>
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<tr>
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<td>161.24</td>
<td>17.12</td>
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<td>−</td>
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<td>−</td>
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</tr>
</tbody>
</table>

Table 2 Various fitting parameters obtained from the electrical resistivity, thermopower and specific heat.

A transition from electron- to hole-like conduction. Thermopower in the positive region is small with a plateau-like feature, which is attributed to the metallic behavior. Below 35 K it decreases with temperature. The decrease of $S$ at low temperatures has been earlier viewed [23] in terms of the phonon drag effect with $S \propto T^3$. However, $S$ in the present case is found to obey a quasi-linear relationship with temperature, ruling out the possibility of the phonon drag effect. On the other hand, behavior of $S$ in the metallic region may be attributed to the magnon drag effect where it roughly follows the magnon specific heat ($\propto T^{3/2}$). With Nb-doping $S$ shifts towards positive values and it is seen from the figure that with 3% Nb, $S$ is positive in the entire temperature range. As we noted earlier, with Nb-doping the average valency at Mn-site shifts towards $+3$, indicating that $e_g$ electrons are created as a result of doping. It seems that, these extra $e_g$ electrons are localized at the site due to non-availability of hopping to the Nb$^{5+}$($d^{10}$) site. As a result of this, there is a decrease in mobility and the shift of $S$ towards positive values can be expected in the Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ system. An estimation of the activation energy in the high temperature insulating regime has been carried out using the relation [16]:

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

(2)

where $E_S$ is the thermopower activation energy and $\alpha$ is a constant related to the kinetic energy of the polarons. Here, $\alpha < 1$ indicates the conduction due to small polarons, whereas $\alpha > 2$ signifies the conduction with large polarons. Basically, the activation energy $E_S$ is the energy required to hop across the barrier between two neighboring sites. From Table 2 it is evident that $E_S$ increases with doping. This is attributed to the increase in the lattice volume of PSMO with Nb-doping, which in turn increases the inter-atomic distance and consequently the barrier height. It is noted that the value of $E_S$ is smaller than $E_p$, suggesting the applicability of the polaron hopping model. Additionally, the obtained value of $\alpha < 1$ in
Table 2 presents the results of thermal conductivity for the pristine, 1%, and 3% Nb-doped samples. The value of thermal conductivity for the studied samples lies in the range of 5–45 mW/cm K. Such a low value of thermal conductivity is attributed to the presence of the JT distortion in the samples [25]. In general, thermal conductivity is a sum of the contributions from the electrons, phonons and magnons (additionally for a magnetic sample). It has been established that the contribution to the thermal conductivity by electrons and magnons in manganites are negligible as compared to the phonons [26]. It is found that the magnitude of $\kappa$ decreases continuously with $x$, implying an increased phonon scattering from static and/or dynamic disorder because of the formation of more JT polarons acting as the scattering centers. The low temperature $\kappa$ behavior can be understood as a result of the defect-induced scattering [27]. With lowering temperature, there is an increase in thermal conductivity in the vicinity of the transition temperature ($T_P$) for the pristine and 1% Nb-doped samples. This rise in $\kappa$ below the transition temperature has been ascribed to the destabilization of the JT polarons, which leads to the reduction in phonon–phonon (ph–ph) scattering [26,28]. However, such a feature has also been reported in magnetic materials such as NiO, CoO and MnO, which do not have any active JT ion [29,30]. Tachibana et al. [19] have recently shown that this anomaly in thermal conductivity in manganites arises from the scattering of phonons with spin fluctuations. In the present case we notice that there is no anomalous feature in the measured thermal conductivity for the 3% Nb-doped sample as it is evident in the electrical resistivity and thermopower, $\kappa$ remains amorphous-like in the whole temperature range. Therefore, we argue that the behavior of $\kappa$ near the transition could also be partly attributed to the phonon scattering with spin fluctuations as suggested in Ref. [19].

In order to further elucidate the presence of spin fluctuations near $T_P$, specific heat measurements of the Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ system were carried out and the results are shown in Fig. 5. For the sake of clarity, the data of doped samples have been shifted with respect to the pristine sample. The specific heat shows a pronounced peak near $T_P$ in the pristine sample due to the occurrence of magnetic ordering. With Nb-doping the peak height decreases and the transition width increases. The magnetic contribution $\Delta C_{mag}$ to the total $C_P$ near the transitions in PSMO can be estimated by subtracting a smooth lattice background fitted far away from the transition. The corresponding entropy change $\Delta S$, evaluated by integrating the area under the $\Delta C_{mag}/T$ versus $T$ curves, is also found to decrease with increasing Nb content. The calculated value of $\Delta S$, given in Table 2, is found to be much smaller than the theoretical value $R \ln 2$ (for the complete alignment of the spins). This gives credence to the presence of the spin fluctuations near $T_P$, in support of the findings in the thermal conductivity measurements.

Fig. 2. Variation of electrical resistivity with temperature for Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ ($x = 0.0, 0.01, 0.03$ and $0.05$) samples. Inset shows the resistivity fitting above $T_P$ using Eq. (1).

Fig. 3. Variation of thermopower with temperature for Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ ($x = 0.0, 0.01$) samples. Inset is for 3% Sb-doped sample.

Fig. 4. Variation of thermal conductivity with temperature for Pr$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Nb$_x$O$_3$ ($x = 0.0, 0.01$ and $0.03$) samples.
Fig. 5. Variation of specific heat with temperature for \( \text{Pr}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Nb}_x\text{O}_3 \) (\( x = 0.0, 0.01 \) and 0.03) samples.

4. Conclusions

Structural, electrical resistivity (\( \rho \)), thermopower (\( S \)), thermal conductivity (\( \kappa \)) and specific heat (\( C_P \)) measurements on \( \text{Pr}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Nb}_x\text{O}_3 \) (\( 0 \leq x \leq 0.05 \)) materials have been systematically studied. The structural and electrical resistivity measurements have been carried out up to 5% Nb-doping, whereas thermal measurements are limited up to 3% Nb-doped sample. The influence of Nb-doping on the structural parameters and electrical resistivity is clearly reflected. The insulator–metal transition temperature of the pristine material \( \text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) shifts to lower temperatures with Nb-doping, with a simultaneous increase in the value of electrical resistivity. The properties of electrical transport of the \( \text{Pr}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Nb}_x \) system can be reasonably understood in the framework of an enhanced electron–phonon interaction with increasing doping content. In addition, the role of the scattering of phonons with spin fluctuations is established in their thermal properties.

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