Electrical, magnetic and thermal properties of Pr$_{0.6-x}$Bi$_x$Sr$_{0.4}$MnO$_3$ manganites

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In the present communication, we report the electrical, magnetic and thermal properties of Bi-doped Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ (PSMO) compounds. These measurements show that the transition temperature decreases with Bi-content. Analyses on the measured electrical resistivity and thermoelcetric power data indicate that the small polaron hopping model is operative in the high temperature paramagnetic phase for all samples. The thermal conductivity $\kappa(T)$ for samples studied in the present work is found to be low which is essentially due to Jahn–Teller (JL) distortion in the samples. It is observed that $\kappa(T)$ is seen to decrease with increase in doping concentration of Bi which is possibly due to the formation of JL polaron which act as scattering centers. From specific heat measurements, we observe reduction in values of entropy change with increase in bismuth content which suggests that the magnetic inhomogeneity increases with Bi substitution.

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1. Introduction

Rare earth manganites of the type ABO$_3$ (A = rare earth) were well-known for several decades, however, they have received immense attention ever since the discovery of colossal magneto-resistance (CMR). In these compounds, electrical resistivity decreases by orders of magnitude upon influence of application of a magnetic field [1–5]. Observation of colossal magneto-resistance (CMR) in pervoskite manganites has been intensively studied, due to their distinctive structural, electrical, thermal and magnetic properties [6]. In the recent years, these materials have received renewed interest due to an exciting property called magneto-caloric effect (MCE). The MCE is defined as the changes in adiabatic temperature or isothermal magnetic entropy of a magnetic material when it is magnetized (or demagnetized). Among the existing CMR manganites, Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) series has been investigated extensively mainly to understand the physics behind phenomena such as CMR, electro-resistance and MCE [7–9]. It is significant to mention that Bi-doped compounds Pr$_{1-x}$Sr$_x$MnO$_3$ exhibit high MCE values and have possible technological importance as refrigerating materials. This system also exhibits both first order as well as second order phase transition. For compounds with $0.2 < x < 0.45$, a second order phase transition from paramagnetic (PM) to ferromagnetic (FM) is seen. On the other hand, the half doped compound $x = 0.5$ exhibits a second order transition (PM to FM) at temperature around 260 K, followed by a first order transition of FM to anti-ferromagnetic transition which is observed at a lower temperature around 125 K. The compounds of Pr$_{1-x}$Sr$_x$MnO$_3$ with $x$ in the vicinity of 0.4 are of enormous importance due to the fact that they exhibit insulator–metal transitions around room temperature.

The family of Bi-based manganites has drawn vast interest essentially because of the physics that lies behind the unusually high charge ordering temperature ($T_{CO} \approx 475$ K) [10]. It has been proposed that the observed anomalously high $T_{CO}$ is perhaps related to the $6s^2$ characteristic of Bi$^{3+}$ which is highly polarized in a certain Bi–O bond direction. An orientation of the $6s^2$ lone pair towards a surrounding anion (O-2p) can possibly produce a local distortion or even hybridization between Bi-6s-orbitals and O-2p-orbitals [11] which may perhaps generate a charge ordered state of series end BSMO compound and hence $e_g$ electrons of Mn$^{3+}$ ions get localized, as a result of this, the mobility of carriers is reduced through Mn$^{3+}$–O–Mn$^{4+}$ networks. In parent compound Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ the Curie temperature $T_{C}$ is found to be about 306 K [12,13]. It is important to mention that from application point of view, Bi-doped manganites have attracted additional

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interest due to its large magneto caloric effect (MCE) which make them possible candidates as refrigerant materials. It may be mentioned that there are two types of magnetic materials which show large MCE viz. those showing first order and second order phase transitions. The compounds studied in the present work are pertaining to the latter type. It may be mentioned that magnetic materials showing second order transition are more suitable for MCE applications than those showing first order transition. In parent compound Pr0.6Sr0.4MnO3 the Curie temperature TC is found to be about 306 K [12,13]. Most of the reports in literature pertain to the compounds with substitution of ions at Mn sites. For example Lu et al. [14] have investigated impurity effects on the stability of a charge-ordered antiferromagnetic state in electron-doped manganite La0.6Ca0.4MnO3 and it is reported that tiny levels of Ru-doping induces ferro-magnetism in these compounds. However, there are few reports on Bi-doped compounds with Pr site substitution even though Bi3+ (1.17 Å) and Pr3+ (1.126 Å) ions have nearly same ionic radii [15,16].

Recently, we have reported comparative studies of Bi-doped compounds Pr0.7−xBi2Sr3−xMnO3 and Pr0.65−xBi2Sr3−xMnO3 [17] and it was found that for the former compounds, both the metal-insulator transition temperature (TMI) and ferromagnetic-paramagnetic transition temperature (TC) increase with increasing Bi concentration. On contrary, for the latter compounds the transition temperatures (TMI and TC) decrease with increasing Bi concentration. This is possibly due to the fact that bigger ionic size of Bi3+ ion dominates and enhances double-exchange (DE) interaction which perhaps result in an insulator transition temperature for Pr0.7−xBi2Sr3−xMnO3 compound. On contrary for Pr0.65−xBi2Sr3−xMnO3 compound, strong hybridization between Bi(6s) and O(2p) orbital is responsible for reduction in TMI and TC in Pr0.7−xBi2Sr3−xMnO3 compound.

There are very few reports on thermal properties for Bi-doped PSMO compounds in the literature. This motivates us to investigate the electrical and magnetic properties of Bi-doped Pr0.6−xBi2Sr0.4−xMnO3 (x = 0, 0.05, 0.1, and 0.15) manganites. It is found that small polaron hopping (SPH) model is operative above the insulator to metal transition temperature in these manganites, whereas electron–electron and electron–magnon scattering processes govern the low temperature metallic behavior. An analysis of thermoelectric power in the ferromagnetic regime suggests that the complicated temperature dependence of thermoelectric power may be understood on the basis of electron–magnon scattering. With increasing temperature, the measured thermal conductivity in the paramagnetic regime is found to increase with increasing temperature, presumably due to local anharmonic distortions associated with small polarons.

2. Experimental

The compounds Pr0.6−xBi2Sr0.4−xMnO3 (0 < x < 0.15) were prepared using solid state reaction method. The starting compounds (Pr2O3, SrCO3, MnO2 and Bi2O3) were taken in the stoichiometric ratio and were mixed well to obtain a homogenous mixture. The mixture was calcined at 1200 °C with three intermediate grindings. The calcined mixtures were taken in the form of pellets and were sintered in air at 1200 °C for 24 h. To confirm the purity of the samples and to determine the lattice parameters, X-ray diffraction (XRD) studies were done using Bruker D8 Advance X-ray diffractometer. The XRD data was analyzed using Rietveld refinement technique to confirm the phase formation as well as to obtain the lattice parameters, space group, and crystal system. Using the Rietveld refinement method we observe that all samples are single phased with orthorhombic structure with Pnma space group. The surface morphology was checked using a Scanning Electron Microscope (SEM- EVO MA18 with Oxford EDS X-Act) attached with Energy Dispersive analysis through X-rays (EDAX) adjustable from 200 V to 30 kV. The SEM patterns demonstrate that all the samples exhibit the granular morphology with average grain size increasing with increase in bismuth concentration. The electrical resistivity measurements were carried out using a superconducting magnetic system (Oxford Spectromag) at magnetic fields 0 T, 4 T, and 8 T over temperature range 4–350 K using four probe method.

Magnetic measurements were carried out in a magnetic field of 80 kOe (7 = 50–350 K) using SQUID VSM dc magneto-meter (Quantum Design MPMS). In the present work, the magnetization was measured under zero-field cooled (ZFC) and field cooled (FC) conditions. Specific heat was measured in 70–350 K with a high resolution ac calorimeter. Thermoelectric power and thermal conductivity measurements were carried out in the temperature 10–350 K in a closed cycle refrigerator using a direct-pulse technique.

3. Results and discussion

3.1. Electrical resistivity and magneto-resistance measurements

Electrical resistivity measurements were carried out at a variety of magnetic fields in the range of 0 – 8 T over a temperature range 4 – 300 K. We first discuss electrical resistivity results with zero external magnetic field. Fig. 1 shows the temperature dependence of electrical resistivity for pure as well as Bi-doped samples. The metal–insulator transition temperature (TMI) is observed at 222 K for the pristine Pr0.6Sr0.4MnO3 (PSMO) sample. With Bi substitution, TMI decreases with increase in Bi content, on contrary, the electrical resistivity increases with Bi concentration. The observed effect is due to the fact that large content of Sr ions possibly increases the tendency of screening of Bi3+ ions. As orientation of the 6s2 lone pair toward a surrounding anion (O2−) produces a local distortion and as a result, the movement of eg electrons through the Mn–O–Mn bridges, is severely reduced.

The electrical resistivity in the low temperature of the metallic phase below TMI is fitted to the following equation.

$$\rho = \rho_0 + \rho_1 T^2 + \rho_2 T^{1.5}$$

(1)

where $\rho_0$ is the residual resistivity arising from the temperature independent processes such as domain wall, grain boundary and vacancies, $\rho_2 T^2$ indicates electron–electron scattering, whereas the $\rho_2 T^{1.5}$ attributes to two magnon scattering process in FM state. The experimental resistivity data are fitted to Eq.(1) and the fitting parameters are given in Table 1. This indicates that in the metallic region the transport mechanism is mainly governed by the electron–electron scattering as the electron–electron scattering term $\rho_2 T^2 = 3.75 \text{ m}\Omega \text{ cm}$ is much larger than the magnon scattering contribution $\rho_2 T^{1.5} = 0.444 \text{ m}\Omega$ at $T = 200 \text{ K}$. It is noted that such a behavior is applicable at any particular temperature we investigated.

In order to explain the variation of electrical resistivity with temperature in the high temperature region, $T > TMI$, we use the adiabatic small polaron model [18] which is given by equation,
\( \rho = \rho_0 T \exp \left( \frac{E_a}{k_B T} \right) \)  

(2)

where \( \rho_0 \) is a constant, \( E_a \) is the activation energy, and \( k_B \) is the Boltzmann constant. Hybridization of Bi\(^{3+}\)-6s\(^2\) orbital and O\(^{2-}\)-2p orbital may produce a charge ordered state of PSMO compound that may create a Jahn–Teller distortion. This causes a strong electron–phonon coupling and hence the formation of polarons, making the strong applicability of the small polaron hopping model \([19,20]\). 

Fig. 2 shows temperature dependent resistivity curves which have been obtained using small polaron model in the high temperature regime for the compounds studied in the present investigation. The activation energy values are obtained (Table 2) using the above equation and it is seen that it decreases with increase in Bi content up to \( x = 0.1 \), however it is found to increase for \( x = 0.15 \). The increase in activation energy may be due to the fact that increase in bismuth concentration lowers the possibility of conduction electron to hop to the neighboring sites \([21]\).

Fig. 3 shows the values of temperature coefficient of resistance (TCR) calculated as \( (1/\rho)(d\rho/dT) \) for the present \( \text{Pr}_{0.6-x}\text{Bi}_x\text{Sr}_{0.4}\text{MnO}_3 \) system. The sharpness of the electrical resistivity near I–M transition is described in terms of the TCR. TCR is the maximum near \( T_{MI} \). For the parent compound, the TCR is found to be 0.27%. It is noted that it increases with increase in bismuth concentration (\( x = 0.10, \) TCR is 0.73%) but decreases with further increase in bismuth content (\( x = 0.15, \) TCR is 0.2%). Comparison of different manganite materials indicates that TCR increases as the insulator–metal transition shifts towards lower temperatures \([9]\).

Fig. 4 depicts the temperature dependent electrical resistivity for pure as well as \( x = 0.15 \) samples without external magnetic field and at magnetic fields of 4 T and 8 T. It can be seen from Fig. 4 that resistivity values decrease with increasing magnetic field and \( T_{MI} \) shifts towards higher temperature region. This may be due to that the delocalized charge carriers induced by applied magnetic field suppress the resistivity which in turn lead to the local ordering of the electron spins. Due to this ordering, the ferromagnetic metallic state might have suppressed the paramagnetic insulating regime resulting in the observed increase in \( T_{MI} \) under applied magnetic field. The temperature dependent magneto-resistance for the compounds \( \text{Pr}_{0.6-x}\text{Bi}_x\text{Sr}_{0.4}\text{MnO}_3 \) (\( x = 0, 0.05, 0.1, \) and 0.15) at magnetic field of 4 T is shown in Fig. 5. Negative MR increases with bismuth content due to the increase in resistivity with increasing bismuth concentration.

### Table 1

Best fit parameters of low temperature resistivity data of \( \text{Pr}_{0.6-x}\text{Bi}_x\text{Sr}_{0.4}\text{MnO}_3 \) (\( x = 0, 0.05, 0.1 \) and 0.15).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \rho_0 ) (( \Omega \text{cm} ))</th>
<th>( \rho_2 ) (( \Omega \text{cm}/\text{K}^2 ))</th>
<th>( \rho_4 ) (( \Omega \text{cm}/\text{K}^4 ))</th>
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<tr>
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<tr>
<td>0.05</td>
<td>( 8.59 \times 10^{-3} )</td>
<td>( 1.09 \times 10^{-7} )</td>
<td>( 5.14 \times 10^{-14} )</td>
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<tr>
<td>0.1</td>
<td>( 1.31 \times 10^{-2} )</td>
<td>( 1.60 \times 10^{-7} )</td>
<td>( 4.96 \times 10^{-14} )</td>
</tr>
<tr>
<td>0.15</td>
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<td>( 3.56 \times 10^{-7} )</td>
<td>( 1.04 \times 10^{-11} )</td>
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### Table 2

Activation energies from electrical resistivity \( (E_a) \) and thermoelectric power \( (E_t) \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( E_a ) (meV)</th>
<th>( E_t ) (meV)</th>
<th>( x )</th>
<th>( W_{E_a} = E_a - E_t )</th>
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Fig. 3. Temperature coefficient of resistance (TCR) variation for the series \( \text{Pr}_{0.6-x}\text{Bi}_x\text{Sr}_{0.4}\text{MnO}_3 \) \( (x = 0, 0.05, 0.1, \) and 0.15).
This may be attributed to the fact that at lower temperatures, the movement of magnetic domains along the magnetic field direction is restricted due to the pinning of domain walls resulting in an incomplete magnetization. With increase in temperature, an increase in thermal energy allows more and more domains to align along the direction of field thereby increases the magnetization. Beyond $T_C$, both $M_{ZFC}$ and $M_{FC}$ curves coincide with each other.

In order to further probe the magnetic properties, magnetization versus magnetic field ($M-H$) measurements were done at 5 K and 200 K. The results are shown in Fig. 7 and one can observe that at 5 K, the magnetization rises piercingly at low magnetic fields and then starts saturating around 16 kOe. Such an observation is primarily due to the rotation of magnetic domains under the action of applied magnetic field [23]. A similar behavior is seen in the $M-H$ curve at 200 K. The values of $T_C$ and isothermal saturation magnetization, $M_s$, for all the samples are given in Table 3.

3.3. Specific heat measurements

Fig. 8 shows temperature dependent specific heat ($C_p$) of Pr$_{0.6-x}$Bi$_x$Sr$_{0.4}$MnO$_3$ ($x = 0, 0.05, 0.1$ and $0.15$). All studied samples show a sharp peak corresponding to the paramagnetic to ferromagnetic transition in its $C_p(T)$ curve. With bismuth substitution, the transition temperature, $T_C$, decreases and the transition width becomes broader with the increase in Bi content. The observed broadening in the $C_p$, anomalies with Bi substitution suggests an increase in magnetic inhomogeneity, most probably due to the weakening of the double-exchange mechanism with Bi$^{3+}$ ion hindering the shift of electrons between Mn$^{3+}$/Mn$^{4+}$ pairs. It is found that low temperature specific heat is less affected by Bi substitution. The magnetic contribution of the specific heat jump $\Delta C_p$ near transition temperature is estimated by subtracting a smooth background, obtained by fitting a lattice background through the data far from the transition. Entropy change $\Delta S$ calculated by integrating the area under $\Delta C_p/T$ versus $T$ curves is shown in inset of Fig. 8. The value of entropy change is less than the theoretical value $R \ln 2$ for a paramagnetic-ferromagnetic transition where $R$ is ideal gas constant, which indicates the magnetic inhomogeneity or incomplete canted spins in the ferromagnetic state of the samples [24]. Reduction in values of entropy change (excess entropy) with increase in bismuth content confirms the increase in magnetic inhomogeneity. The calculated value of $\Delta S$ is also given in Table 3.

3.4. Thermoelectric power and thermal conductivity measurements

Fig. 9 shows the variation of thermoelectric power ($S$) with temperature for the studied samples. The pristine sample shows a slope change at around 310 K (shown by arrows) which is suppressed by bismuth substitution. Large negative $S$ value at high temperature and small positive $S$ value at low temperature indicate the insulating and metallic nature in these temperature regions, respectively. The negative sign of $S$ suggests that the n-type conduction dominates the thermoelectric transport in these manganites. In metallic region the negative thermoelectric power. With bismuth substitution, $S$ is found to be negative in the entire temperature range, indicating that the localization of $e_g$ electrons may be presence as magnetic polarons. As bismuth content increases, orientation of the $6s^2$ lone pair toward a surrounding anion ($O^{2-}$) can produce a local distortion or even a hybridization between $6s$-Bi-orbitals and $2p$-O-orbitals which increase the electron–phonon coupling. The temperature

---

**Table 3**

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_C$ (K)</th>
<th>$M_s$ (emu/cm$^3$)</th>
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<tr>
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<tr>
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</tr>
<tr>
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<td>200</td>
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</table>
dependence of thermoelectric power in the insulating regime is described by Eq. (3) in the framework of polaron model,

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

where \( E_S \) is the thermoelectric power activation energy and \( \alpha \) is a constant related to the kinetic energy of the polarons. From the evaluation of resistivity activation energy \( E_q \), it is found that \( E_q \) is much higher than \( E_S \), suggesting applicability of small polaron hopping model in the insulating region. And also \( \alpha < 1 \) suggests a conduction due to small polarons in these manganites. The deduced polaron hopping energy \( (\Delta W_H) \) from the difference of \( E_q \) and \( E_S \) increases with bismuth substitution, and \( E_S \) and \( \alpha \) values are given in Table 2. The fitted curve to Eq. (3) of pure sample is shown in inset (ii) of Fig. 9. From the electrical resistivity data, we had shown that the contribution from electron–magnon scattering is less than that due to electron–electron scattering. It is still possible that other scattering channels such as spin wave scattering may be present. To verify these arguments, thermoelectric power data in FM region is

![Fig. 6. Magnetization variation with temperature of the Pr\(_{0.6-x}\)Bi\(_x\)Sr\(_{0.4}\)MnO\(_3\) (a) for \( x = 0 \), (b) for \( x = 0.05 \), (c) for \( x = 0.1 \), and (d) for \( x = 0.15 \).]

![Fig. 7. Magnetization vs. applied magnetic field of Pr\(_{0.6-x}\)Bi\(_x\)Sr\(_{0.4}\)MnO\(_3\) for \( x = 0, 0.05, 0.1, \) and 0.15 series (a) at 5 K (b) at 200 K.]

\[ \text{Table 3} \]

Curie temperature \( (T_C) \), saturation magnetization \( (M_S) \) of Pr\(_{0.6-x}\)Bi\(_x\)Sr\(_{0.4}\)MnO\(_3\) \((x = 0, 0.05, 0.1 \) and 0.15).
analyzed by considering several factors such as impurity, band structure, electron–magnon scattering and spin wave fluctuations, and thus the measured $S(T)$ is given by the expression,

$$S(T) = S_0 + S_{3/2}T^{3/2} + S_4T^4$$  \hspace{0.5cm} (4)

where $S_0\ (S at T = 0 K)$ has no physical origin, $S_{3/2}T^{3/2}$ is related to electron–magnon scattering and $S_4T^4$ is due to spin wave fluctuations in the FM phase. The fitted curve to Eq. (4) of pure sample is shown in inset (i) of Fig. 9. From the fitting parameters listed in Table 4, it is clear that $S_{3/2}$ is five orders of magnitude larger than $S_4$, implying that electron–magnon scattering is the dominant mechanism for thermoelectric transport in FM metallic regime. The generation of magnetic polaron is due to the hybridization of Bi$^{3+}$–6S$^2$ orbital and O$^{2-}$–2p orbital [24].

Fig. 10 shows the temperature dependent thermal conductivity $\kappa(T)$ of Pr$_{0.6}$–BixSr$_{0.4}$MnO$_3$ ($x = 0, 0.05, 0.1$ and $0.15$) samples. The transition temperature determined from $\kappa(T)$ is shown by arrows in Fig. 10. The decreasing trend of $T_C$ with Bi$^{3+}$ ion substitution is consistent with electrical, magnetic and other thermal measurements. The value of thermal conductivity for the studied samples lies in the range of 5–45 mW/cm K. Such a low value of $\kappa$ is attributed to the presence of the JT distortion in these manganites [26,27]. The magnitude of $\kappa(T)$ decreases with $x$ suggesting an increased phonon scattering from JT distortion, because the formation of JT polarons may act as scattering centers in the studied samples. Besides, it is seen that $\kappa(T)$ increases with increasing temperature in the paramagnetic phase, presumably owing to the formation of magnetic polarons by Bi$^{3+}$–6S$^2$ orbital screening effect. On the other hand, the rise in $\kappa(T)$ below transition temperature is due to delocalization of charge carrier or suppression of magnetic polarons. The low temperature peak near 100 K can be ascribed to a crossover from phonon–phonon to defect-limited scattering.

Since the thermal conductivity of solids are expected to closely follow Wiedemann–Franz’s law over a wide temperature range, the electronic thermal conductivity can thus be estimated by using $\kappa_e/\kappa = L_0$. Here $\rho$ is the dc electric resistivity and the Lorentz number $L_0 = 2.45 \times 10^{-8}$ W Ω K$^{-2}$. From this estimation, it is found that $\kappa_e$ contributes less than 1% to the total thermal conductivity. We thus can safely conclude that the measured thermal conductivity is mainly due to lattice phonons rather than charge carriers in these manganites.

4. Conclusions

The structural, electrical, magnetic and thermal properties of Pr$_{0.6}$–BixSr$_{0.4}$MnO$_3$ ($x = 0, 0.05, 0.1$ and $0.15$) have been studied. All the samples are single phased with Pnma space group. It is seen that unit cell volume decreases with increasing bismuth concentration. The electrical and magnetic investigations show that both metal–insulator transition and Curie temperature decrease with increase in bismuth content. Large magnetoresistance of 90% at 8 T field is achieved in the low-temperature region for $x = 0$ sample. Analyses of the electrical transport data found that small polaron hopping (SPH) model is operative above the insulator to metal transition temperature in these manganites, whereas electron–electron and electron–magnon scattering processes govern the low temperature metallic behavior. The observed broadening in the specific heat anomalies with Bi substitution suggests an increase in magnetic inhomogeneity. The measured thermal conductivity increases with increasing temperature in the paramagnetic phase, presumably due to the formation of magnetic polarons. The magnitude of thermal conductivity is found to decrease with Bi content, indicating an increased phonon scattering from Jahn–Teller distortion.

![Fig. 8. Variation of specific heat with temperature of Pr$_{0.6}$–BixSr$_{0.4}$MnO$_3$ ($x = 0, 0.05, 0.1$ and $0.15$) series.](image)

![Fig. 9. Variation of thermoelectric power with temperature of Pr$_{0.6}$–BixSr$_{0.4}$MnO$_3$ ($x = 0, 0.05, 0.1$ and $0.15$) series. Inset (i) shows the fitting above $T_C$ and inset (ii) shows the fitting below $T_C$.](image)

![Fig. 10. Variation of thermal conductivity with temperature of Pr$_{0.6}$–BixSr$_{0.4}$MnO$_3$ ($x = 0, 0.05, 0.1$ and $0.15$) series.](image)

Table 4

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