

# Electrical conduction and thermal properties of Bi-doped $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ manganite

MAMATHA D DAIVAJNA, NEERAJ KUMAR<sup>†</sup>, BHASKER GAHTORI<sup>‡</sup>, V P S AWANA<sup>‡</sup>,  
Y K KUO<sup>‡</sup> and ASHOK RAO<sup>#,\*</sup>

Department of Physics, Manipal Institute of Technology, Manipal University, Manipal 576 104, India

<sup>†</sup>Department of Physics, University of Trento, Trento, Italy

<sup>‡</sup>Superconductivity and Cryogenics Division, National Physical Laboratory (CSIR), Dr K S Krishnan Marg, New Delhi 110 012, India

<sup>#</sup>Department of Physics, National Dong-Hwa University, Hualien 974, Taiwan

MS received 10 September 2012; revised 18 October 2012

**Abstract.** Electrical and thermal properties of Bi-doped  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (PSMO) compounds are reported here. It is observed that Bi-doped PSMO compounds follow variable range conduction mechanism. Specific heat, thermal conductivity and thermo-power measurements show that larger Bi-ion, in place of smaller Pr ion, enhances their transition temperatures ( $T_{\text{MI}}$ ,  $T_{\text{C}}$ ,  $T_{\text{CP}}$ ). Thermo-power measurements further strengthen our conclusion for the presence of magnetic polaron, generated due to hybridization of  $\text{Bi}^{3+}-6s^2$  and  $\text{O}^{2-}-2p$  orbital and polaronic conduction mechanism.

**Keywords.** Magnetic polaron; variable range conduction; thermal measurement.

## 1. Introduction

Since last decade, manganites with the general formula,  $\text{A}_{1-x}\text{A}'_x\text{MnO}_3$  (where A = rare-earth element and A' = alkaline-earth metals), are intense subject of research from the point of basic physics to understand strongly correlated electron system and technological applications because of large value of magneto-resistance and magneto-caloric effect (Rao and Raveau 1998; Zemini *et al* 2009; Rostamnejadi *et al* 2011). The promise of coupling between  $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$  ions proposed by Zener (1951) can be counter balanced by choosing either “A” or “Mn” site substitution and transition temperature ( $T_{\text{C}}$ ,  $T_{\text{MI}}$ ) can be achieved at room temperature (Zener 1951; Awana *et al* 2010). Current research suggests that these materials do not have single phase, they rather contain mixed magnetic phases which suppress/enhance with temperature near to its  $T_{\text{C}}$ ,  $T_{\text{MI}}$  and believed to be the key origin of colossal magneto-resistance (CMR) (Uehara *et al* 1999). Recently, Barik and Mahendiran (2010) observed  $\sim 100\%$  MR and magnetic hysteresis in Bi-doped  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  compounds. The unusual behaviour is because of co-existing ferromagnetic (FM) and antiferromagnetic (AFM) matrices (Barik and Mahendiran 2010). It is important to mention that Bi-doped manganites have attracted extra attention due to its large magneto-caloric effect (MCE), which are possible candidates as refrigerant materials. The end compound (BSMO) is a charge order AFM and it is believed that in

Bi-doped manganites, melting of this CO–AFM state can cause large MCE (Kurian and Singh 2011). Gencer *et al* (2005) reported an entropy ( $\Delta S$ ) of  $\sim 3.5$  J/kgK under 1 T field in  $\text{La}_{0.62}\text{Bi}_{0.05}\text{Ca}_{0.33}\text{MnO}_3$  compound and in a similar manner Bi-doping in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  enhances magnetic refrigeration capacity and attains higher value ( $\Delta S$ ) of  $\sim 5.02$  J/kgK (Gencer *et al* 2005; Barik and Mahendiran 2010).  $\text{Bi}^{3+}$  ion at Mn site have been studied several times, but there are less reports on ‘A’ site substitution even though  $\text{Bi}^{3+}$  (1.17 Å) and  $\text{Pr}^{3+}$  (1.126 Å) ions have nearly same ionic radii (Kammoun *et al* 2008; Zhang *et al* 2010). Recently, we have reported electrical and magnetic properties of Bi-doped PSMO compound (Neeraj Kumar *et al* 2010). Little work seems to have been done on the thermal properties for Bi-doped PSMO compounds. Thus, it was highly desirable to carry out thermal measurements on Bi-doped PSMO compounds. In this communication, we report thermal properties (specific heat, thermo-power and thermal conductivity) of Bi-doped compound,  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$ .

## 2. Experimental

The samples in the series with nominal composition,  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ), were prepared by conventional solid-state reaction method. Sample synthesis details of these compounds are given elsewhere (Neeraj Kumar *et al* 2010). Electrical resistivity as a function of temperature was measured using conventional four-probe method. Thermal conductivity and thermo-power measurements were carried out simultaneously in the

\*Author for correspondence (ashokanu\_rao@rediffmail.com)

temperature range 10–350 K using a direct pulse technique. Specific heat measurements were performed in the temperature range 100–350 K using an a.c. calorimeter. Details of thermal measurement techniques are given elsewhere (Agarwal *et al* 2010).

### 3. Results and discussion

#### 3.1 Conduction mechanism above $T_{MI}$

In our recent communication (Neeraj Kumar *et al* 2010), we had reported that with the increase in Bi-doping concentration, metal–insulator transition temperature ( $T_{MI}$ ) increases and a second peak arises near 200 K along with increase in resistivity (Neeraj Kumar *et al* 2010). Here, we are elaborating more about conduction mechanism to support the presence of magnetic polaron.

Recently, Liu *et al* (2002) observed that Fe doping in PSMO generates magnetic polaron and follows variable-range conduction mechanism instead of small-range conduction. Figure 1 (for clarity, data is offset) shows fitted data for Holstein’s model (small range hopping conduction) (Alexandrov and Yavidov 2004) in adiabatic regime above  $T \sim \theta_D/2$ :

$$\rho = \rho_0 T \exp(E_\rho/k_B T), \quad (1)$$

where  $\rho_0$  is a constant,  $E_\rho$  the polaron hopping energy and  $k_B$  the Boltzmann constant. Above Debye temperature ( $\theta_D$ ), conduction mechanism is accounted for thermally activated polaron hopping. The calculated values of polaron hopping energy ( $E_\rho$ ) and Debye temperature ( $\theta_D$ ) are listed in table 1.

The behaviour of activation energy can be understood in terms of larger ionic radii and  $\text{Bi}^{3+}-6s^2$  orbital and  $\text{O}^{2-}-2p$  orbital hybridization. In manganites, conduction takes place between  $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$  networks and in the studied

compounds  $\text{Bi}^{3+}$  ion doping does not affect  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio, it is constant (70:30) for all the compositions. Larger ionic radii of  $\text{Bi}^{3+}$  ion further supports DE conduction mechanism, which results in a decrease in polaron activation energy for  $x = 0.15$ . For  $x = 0.25$ , an increase in activation energy behaviour can be understood in terms of screening effect of  $\text{Bi}^{3+}-6s^2$  orbital (Kurian and Singh 2011). As  $\text{Bi}^{3+}-6s^2$  orbital orients towards  $\text{O}^{2-}-2p$  orbital, it produces a local distortion and hence,  $e_g$  electron of  $\text{Mn}^{3+}$  ions get localized, as a result mobility of carriers are reduced through  $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$  networks. Therefore, hybridization of  $\text{Bi}^{3+}-6s^2$  and  $\text{O}^{2-}-2p$  orbitals may generate lattice polaron/magnetic polaron in  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.25$ ) compounds that localizes the electron, which is possibly the reason for increase in activation energy. Figure 1 also shows fitted resistivity data using variable range hopping model (VRH) (Mott 1993).

$$\rho = \rho_0 \exp(T_0/T)^{1/4}, \quad (2)$$

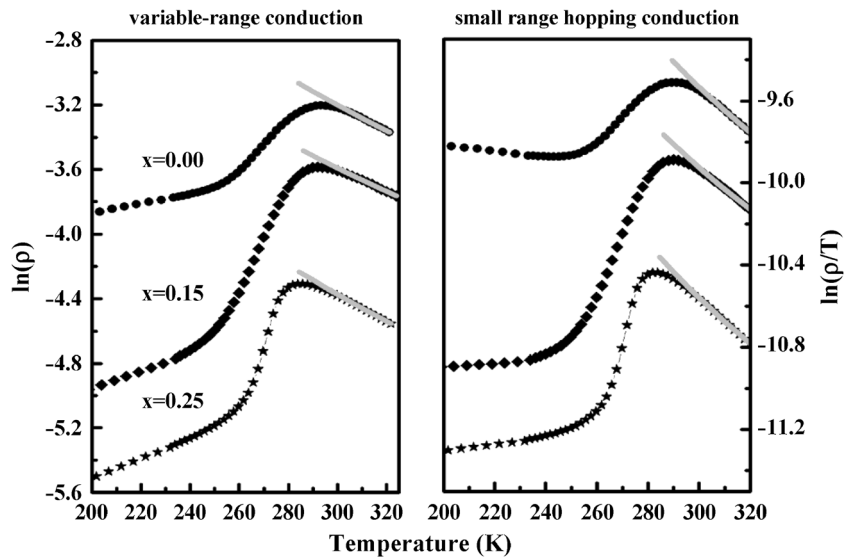
where  $T_0$  is related to spatial extension of localized states and density of states and is listed in table 1.

$T_0$  reflects similar behaviour as small-range electron hopping energy. Both models are fitted well up to  $T_{MI}$ , however, all samples seem to follow variable-range hopping model in a little more satisfactory way based on fitting reduced  $\chi$ -factor. The variable range conduction mechanism supports the presence of magnetic polarons in our studied compounds.

#### 3.2 Magneto-resistance(MR) measurement

Magneto-resistance (MR) is defined as the relative change in the electrical resistivity of any material by the application of magnetic field and is formulated as:

$$\text{MR}\% = [(\rho_H - \rho_0) / (\rho_H)] * 100. \quad (3)$$



**Figure 1.** Temperature dependence of  $\ln(\rho)$  for various samples using small range polaron and variable range polaron models.

We have performed MR measurements on varying magnetic fields from 0–8 Tesla of  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ) compounds. It is observed that MR increases with applied magnetic field for all the samples which is due to spontaneous alignment of Mn spins which allows delocalization of  $e_g$  electron thereby decreasing the resistance. Figure 2 shows MR curves of Bi-doped PSMO compound between 0 and 300 K at 6 T. It is observed that MR decreases with increase in Bi concentration.

### 3.3 Thermal measurement

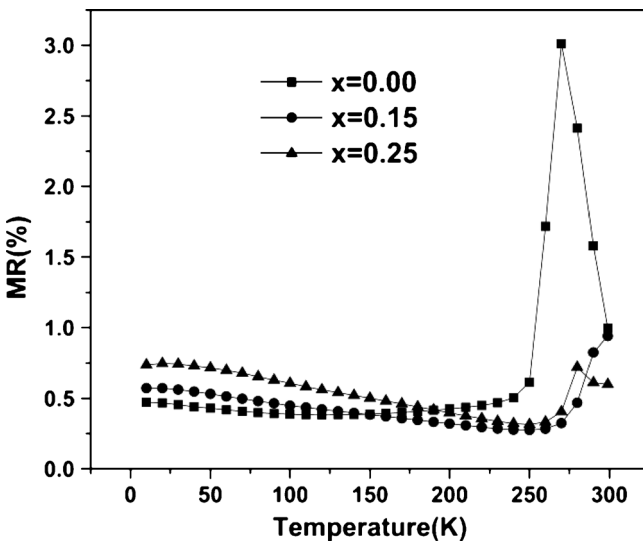
**3.3a Specific heat measurement:** Figure 3 shows specific heat ( $C_p$ ) of pristine and Bi-doped PSMO compounds between 100 and 350 K. For the parent compound,  $\lambda$ -shaped peak is observed near 260 K, which is associated with phase transition. The sharpness of peak indicates uniformity and homogeneity of single-phase parent sample. The specific heat measurements show that the transition temperature ( $T_{cp}$ ) increases with Bi-doping. These results are consistent with the electrical and magnetic studies (Neeraj Kumar

*et al* 2010). For Bi-doped compounds, no anomaly is observed in specific heat, however, the broadness in  $\lambda$  peak possibly indicates magnetic inhomogeneity in doped compound samples. The specific heat jump,  $\Delta C_{mag}$ , near the transitions were estimated by subtracting a smooth lattice background fitted far away from the transitions. Inset of figure 2 shows temperature dependence of  $\Delta C_{mag}/T$  for the presently studied compounds. An important parameter entropy ( $\Delta S$ ) associated with FM transition, can be obtained by integrating the area under  $\Delta C_{mag}/T$  vs  $T$  curves. It is satisfactory to note that the present results are in agreement with those reported for parent compound (Kammoun *et al* 2008; Agarwal *et al* 2010). With Bi-doping, entropy slightly decreases from 2.06 J/mol K (pristine sample) to 1.63, 1.45 J/mol K for  $x = 0.15$  and  $0.25$  compounds, respectively.

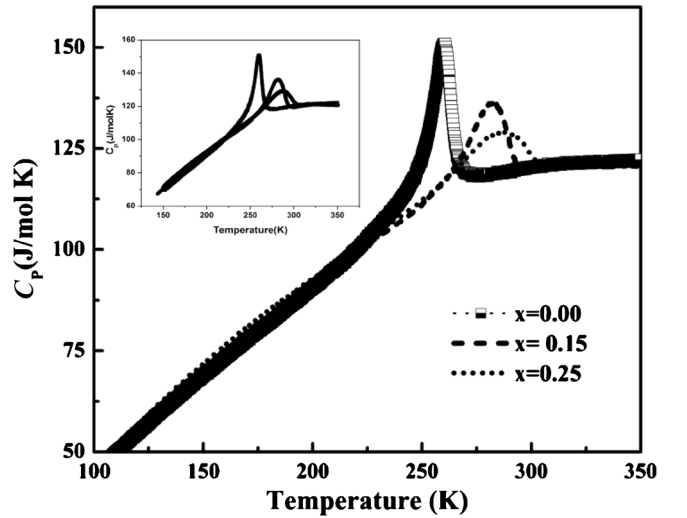
**3.3b Thermo-power and thermal conductivity measurement:** Figure 4 shows temperature dependence of thermo-power for the presently studied  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ) compounds and it further confirms that  $\text{Bi}^{3+}$  ion increases transition temperature.

**Table 1.** Fitting parameters of  $\rho$  vs  $T$  curves characterizing small range polaron and variable range fits and calculated parameters from specific heat ( $C_p$ ) measurement.

$\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$	$T_{IM}$ (K)	$\theta_D$ (K)	Small-range activation energy ( $E_p$ ) (meV)	Variable range $T_0^*10^6$ (K)	$T_{cp}$ (K)	$\Delta S$
$x = 0.00$	284.46	604.10	102.15	4.90	260	2.06
$x = 0.15$	293.29	604.16	87.11	2.01	282	1.63
$x = 0.25$	294.04	606.44	96.14	3.51	285	1.45



**Figure 2.** Magneto-resistance (MR) vs temperature curves for series  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ) at 6 T.

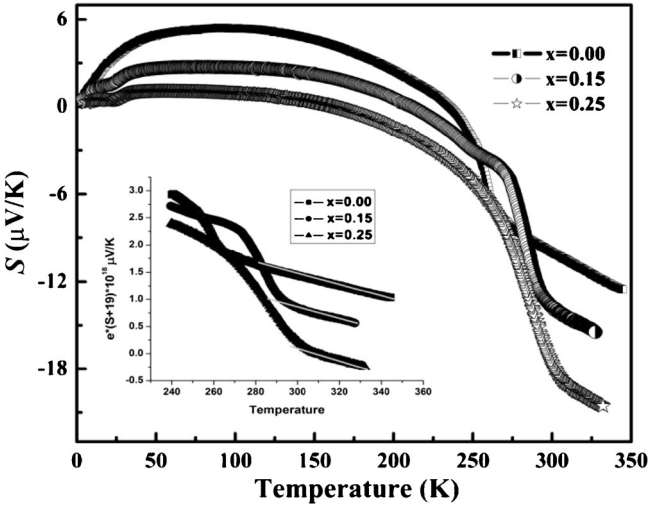


**Figure 3.** Specific heat vs temperature ( $C_p-T$ ) curves for series  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ) compounds. Inset shows  $\Delta C_{mag}/T$  vs  $T$  curves for series compounds.

Low temperature thermoelectric power ( $S$ ) is positive for all compounds; moreover with temperature, it changes sign and becomes negative around 237 K for the parent compound and at 215 and 166 K, respectively for  $x = 0.15$  and  $0.25$  doping concentrations; thereby signifying electron to hole-like conduction. In low temperature regime,  $S(T)$  is linear and it becomes nonlinear around  $T > 20$  K, which is due to electron–magnon scattering. With  $\text{Bi}^{3+}$  ion doping, entire  $S$  shifts towards negative value which indicates localization of  $e_g$  electron, which may be due to magnetic polaron. Recently, Jaime *et al* (1996) reported the presence of magnetic polaron in LCMO films evident by thermo-power study. For the confirmation of magnetic polaron, we have fitted our data with Chaikin and Beni (1976) model proposed for polaronic conduction

$$S = \frac{k_B}{e} \left[ \frac{\varepsilon_0}{k_B T} \right] - \ln \left( \frac{5}{4} \right) - \ln \left( \frac{c(1-c)}{(1-2c)^2} \right),$$

where  $\varepsilon_0$  is the thermo-power activation energy, second term  $\sim -19 \mu\text{V/K}$  contributes configurational entropy of hole moving in spin-2 background having spin 3/2 and third term represents mixing entropy with near neighbour repulsion (number of ways that holes ( $x = 0.30$  in our case) can be arranged between Mn sites). Inset of figure 3 shows fitted



**Figure 4.** Thermo-power vs temperature ( $S$ – $T$ ) curves for series  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ) compounds.

thermo-power data. The calculated values of activation energies ( $\varepsilon_0$ ,  $W_H - J = E_\rho - \varepsilon_0$ ),  $c$  and polaron binding energy ( $E_P = 2W_H$ ) along with transition temperature ( $T_S$ ) are listed in table 2.

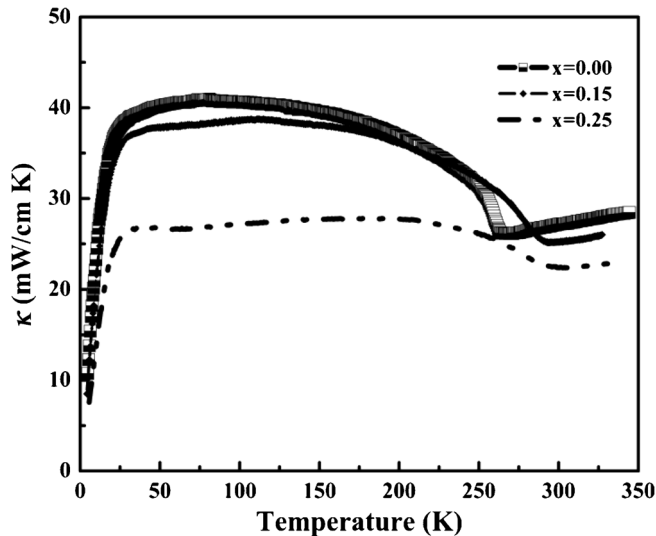
$E_P$  and  $W_H$ , both increase with  $\text{Bi}^{3+}$  ion doping and this suggests increase in  $e$ -ph coupling. Above transition temperature ( $T_S$ ),  $S$  for parent compound is  $\sim -11 \mu\text{V/K}$  and becomes more negative with a value of  $\sim -19 \mu\text{V/K}$  for  $x = 0.25$  and can be understood in terms of enhanced  $e$ -ph coupling. Earlier for LCMO and LSMO compounds, Mahendiran *et al* (1996) observed similar effect and found that thermo-power becomes more negative as one increases  $\text{Mn}^{4+}$  ion ratio or in other sense by increasing  $e$ -ph coupling. For the presently studied compounds,  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ion ratio (70/30%) is constant, the only possibility is that  $\text{Bi}^{3+}$  ion enhances  $e$ -ph coupling by hybridization between  $\text{Bi}^{3+}-6s^2$  and  $\text{O}^{2-}-2p$  orbitals as strong coupling can be seen in series end  $\text{Bi}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  compound (Kurian and Singh 2011).

In brief summary, low reduced  $\chi^2$  value and observed doping level ( $c$ ) indicate the reliability of fitting with this model and further strengthens our view for the presence of magnetic polaron that is generated due to hybridization of  $\text{Bi}^{3+}-6s^2$  and  $\text{O}^{2-}-2p$  orbitals. Further to understand the effect of doping on thermal conductivity ( $\kappa$ ) of all studied compounds, we have characterized these doped compounds between 10 and 350 K temperature regimes as shown in figure 5. Like other electrical, magnetic and thermal measurements,  $\kappa$  also confirms enhancement of transition temperature with  $\text{Bi}^{3+}$  ion doping. At room temperature, the observed magnitude of  $\kappa$  is  $\sim 27.4, 25.4$  and  $22.6 \text{ mW/cm K}$ , these values are one order smaller than high temperature superconductors and are well in agreement with previous reports (Kammoun *et al* 2008; Agarwal *et al* 2010). Such small  $\kappa$  values increasing with temperature are well studied in manganites and can be explained in terms of magnetic polaron or dynamic JT distortion (Cohn *et al* 1997; Visser *et al* 1997).

Keeping in mind, all other measurements (electric, magnetic and thermal), we can confidently state that  $\kappa$  behaviour ( $\kappa$  decreases with doping concentration) in paramagnetic phase is due to magnetic polaron generated by  $\text{Bi}^{3+}-6s^2$  orbital screening effect. As we approach  $T_c$  or  $T_{\text{MI}}$ , thermal conductivity ( $\kappa$ ) increases ( $41.0, 38.8$  and  $27.5 \text{ mW/cm K}$  at 125 K) due to strong localization/large screening effect for  $x = 0.25$ ,  $\kappa$  does not increase sharply and broad transitions are similar to electrical and magnetic measurements (Kumar *et al* 2010).

**Table 2.** Fitting parameters of thermo-power vs temperature ( $S$ – $T$ ) curves characterizing Chaikin and Bani model fits in high temperature regime and observed transition temperature in  $S$ – $T$  and  $k$ – $T$  measurements.

$\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$	$\varepsilon_0$ (meV)	$c$	$W_H - J$ (meV)	$E_P$ (meV)	$T_S$ (K)	$T_k$ (K)
$x = 0.00$	5.79	0.287	96.36	192.72	$\sim 263$	$\sim 264$
$x = 0.15$	8.74	0.288	78.37	156.74	$\sim 291$	$\sim 292$
$x = 0.25$	6.64	0.299	89.50	179.00	$\sim 295$	$\sim 295$



**Figure 5.** Thermal conductivity vs temperature ( $\kappa - T$ ) curves for series  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ) compounds.

#### 4. Conclusions

Electrical conduction and thermal properties of  $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.00, 0.15$  and  $0.25$ ) compounds are studied. The electrical resistivity, specific heat, thermopower and thermal conductivity measurements, confirm that larger  $\text{Bi}^{3+}$  ions enhance transition temperature and also contributes in DE conduction mechanism, it is further established that  $\text{Bi}^{3+}-6s^2$  orbital screening effect generates magnetic polaron that localizes  $e_g$  electron which results in broad transition widths.

#### Acknowledgements

One of the authors (NK) is thankful to the Council of Scientific and Industrial Research (CSIR), India and further acknowledges the financial support to carry out research work at NPL. (AR) is grateful to the UGC-DAE Consortium for Scientific Research, Indore, for financial support under the scheme CSR-I/CSR/43/1462. The authors are thankful

to Dr Rajiv Rawat, UGC-DAE CSR, Indore, for magneto-resistance measurements. Thermal measurements were supported by the National Science Council of Taiwan.

#### References

- Agarwal S K, Neeraj Kumar, Neeraj Panwar, Gahtori Bhasker, Rao Ashok, Chang P C and Kuo Y K 2010 *Solid State Commun.* **150** 684
- Alexandrov A S and Yavidov B Ya 2004 *Phys. Rev. B* **69** 07310
- Awana V P S *et al* 2010 *J. Appl. Phys.* **107** 09D723
- Barik S K and Mahendiran R 2010 *J. Appl. Phys.* **107** 093906
- Chaikin P M and Beni G 1976 *Phys. Rev. B* **13** 647
- Cohn J L, Neumeier J J, Popoviciu C P, McClellan K J and Leventouri Th 1997 *Phys. Rev. B* **56** R8495
- Gencer H, Atalay S, Adiguzel H I and Kolat V S 2005 *Phys. B. Condens. Matter* **357** 326
- Jaime M, Salamon M B, Rubinstein M, Treece R E, Horwitz J S and Chrisey D B 1996 *Phys. Rev. B* **54** 11914
- Kammoun W, Cheikhrouhou-Koubaa W, Boujelben W and Cheikhrouhou A 2008 *J. Alloys Compds* **452** 195
- Kurian Joji and Singh R 2011 *J. Alloys Compds* **509** 5127
- Liu J M, Yu T, Huang Q, Li J, Shen Z X and Ong C K 2002 *J. Phys. Condens. Matter* **14** L141
- Mahendiran R, Tiwary S K, Roychaudhuri A K, Ramakrishnan T V, Mahesh R, Rangavittal N and Rao C N R 1996 *Phys. Rev. B* **53** 3348
- Mott N F 1993 *Conduction in non-crystalline materials* (Oxford: Clarendon Press) 2<sup>nd</sup> Edn
- Neeraj Kumar, Kishan H, Rao A and Awana V P S 2010 *J. Alloys Compds* **504** L39
- Rao C N R and Raveau B 1998 *Colossal magneto-resistance charge ordering and related properties of manganese oxide* (Singapore: World Scientific)
- Rostamnejadi A, Venkatesan M, Kameli P, Salamati H and Coey J M D 2011 *J. Magn. Magn. Mater.* **323** 2214
- Uehara M, Mori S, Chen C H and Cheong S W 1999 *Nature* **399** 560
- Visser D W, Ramirez A P and Subramanian M A 1997 *Phys. Rev. Lett.* **78** 3947
- Zemini S, Baazaoui M, Dhahri Ja, Vincent H and Oumezzine M 2009 *Mater. Lett.* **63** 489
- Zener C 1951 *Phys. Rev.* **82** 403
- Zhang R R, Kuang G L, Zhao B C and Sun Y P 2010 *Solid State Commun.* **150** 209