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Colossal thermoelectric power in Gd-Sr manganites

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Abstract – Manganites belonging to the series $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$ and 0.5) were prepared by wet solid-state reaction and their thermoelectric power was evaluated. Thermoelectric power measurements revealed a peak value at ~ 40 K. All the samples exhibited a colossal thermopower at ~ 40 K and in that $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ exhibited a maximum value of ~ 35 mV/K, which is the largest reported for these class of materials at this temperature. Temperature-dependent magnetisation measurements showed that the samples exhibit a phase transition from paramagnetic to spin-glass-like state at these temperatures. Plausible mechanisms responsible for the observed colossal thermoelectric power in Gd-Sr manganites are discussed.

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The thermoelectric effect is the generation of an electric field due to a thermal gradient, and the rate of change of thermoelectric voltage with temperature is called the thermoelectric power or Seebeck coefficient [1]. Possible applications of thermoelectric materials are in eco-friendly refrigeration and in electrical power generation [2–4]. The efficiency of a thermoelectric conversion is determined by the figure of merit Z which can be written in the form $Z = Q^2\sigma/K$, where Q is the Seebeck coefficient, σ is the electrical conductivity and K is the thermal conductivity. Accordingly, large Seebeck coefficient, high electrical conductivity and low thermal conductivity are prerequisites for materials with potential for applications. Metals are poor thermoelectric materials because they possess small values of Seebeck coefficient. Insulators display large values of Seebeck coefficient, but are poor electrical conductors and are not in demand. However semiconductors with an electron density of $\sim 10^{19}/\text{cm}^3$ are considered as ideal thermoelectric materials [3].

Abraham Ioffe in 1956 theoretically predicted that doped semiconductors could exhibit a much larger value of Seebeck coefficient. Eventually this led to the discovery

of a large thermoelectric power for binary semiconductors of the form Bi_2Te_3 at room temperature [5,6]. Normal broad band semiconductors, rattling semiconductors with skutterudite crystal structure, correlated metals and semiconductors, Kondo insulators and semiconductor quantum wells were also found to be promising thermoelectric materials [3,4,7,8]. Large value of thermoelectric power of the order of 10 mV/K at ~ 20 K was exhibited by pure germanium single crystals [9,10].

A survey of the literature reveals that SrTiO_3 , a metal oxide with cubic perovskite structure, is a good thermoelectric material [2,11,12], while rare-earth intermetallic compounds, whose $4f$ levels are close to the Fermi energy and by virtue of their high density of states near the Fermi energy, scatter most of the conduction electrons, are also considered to be good thermoelectric materials. Therefore, materials, with large number of atoms per unit cell, large average atomic mass and large coordination number per unit atom, are likely to display large thermoelectric power [3]. So perovskite structured manganites (mixed valence manganese oxides with both rare-earth and alkaline-earth metallic cations) are capable of displaying large value of Seebeck coefficient. Maignan *et al.* [13] reported that perovskite manganite is a potential material for thermoelectric applications. High bandwidth manganites like $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, though they

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posses large value of electrical conductivity, display very small values of Seebeck coefficient. However, low band width manganites like $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ can be a material with potential for displaying large Seebeck coefficient. Temperature-dependent electronic and magnetic properties of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ were previously addressed by other researchers [14–16]. Colossal magnetoresistance in $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ was reported by García-Landa *et al.* [14]. Irreversibility and sharp anomalies in the magnetostriction, magnetisation and magnetoresistance at low temperatures were attributed to the occurrence of a charge ordered state. For temperatures less than 42 K it was found that the charge ordered state coexists with a cluster-glass state and this was supported by neutron scattering experiments. Terai *et al.* [15] observed a spin-glass behavior for this compound at low temperatures. Recently Wagh *et al.* [16] reported a large magnetoresistance for single-crystal $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ at 45 K in a field of 110 kOe. So it is presumed that manganites belonging to the series $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ may also exhibit large thermoelectric power because of their unusual electronic and magnetic transformations at low temperatures. Manganites belonging to the series $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$ and 0.5) were prepared, and were then subjected to thermoelectric measurements. To our surprise a colossal thermoelectric power was exhibited by manganites having the composition $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$ and 0.5). Further, magnetisation measurements were also conducted on these samples and the results are reported here.

Samples were prepared according to the following procedure. Stoichiometric amounts of Gd_2O_3 , SrCO_3 and MnO_2 were mixed in concentrated HNO_3 . The solution was heated, boiling off the excess HNO_3 . The precursor was then calcinated in air at 900°C overnight. The remaining powder was pressed into pellets and sintered at 1200°C in air for 72 hrs [17]. The samples were analyzed by means of X-Ray Powder Diffractometer (Rigaku Dmax - C) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The thermoelectric power of these compounds was determined by employing a DC differential technique in the temperature range of 5 K–300 K in a home made set up at IUC-DAEF, Indore, India. Field-cooled (FC) and zero-field-cooled (ZFC) measurements on $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ were carried out in a Quantum Design SQUID VSM in the temperature range of 10 K–300 K at two different magnetic fields of 50 Oe and 200 Oe. M - H measurements were also recorded for the same sample at temperatures of 10 K, 40 K and 250 K in the field range from -3 T to 3 T .

Figure 1 shows the XRD pattern of the sample $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$. The observed peaks were indexed on the basis of an orthorhombically distorted perovskite structure (space group Pbnm), which is in agreement with previous reports [17,18].

The results obtained after measuring the thermoelectric power are shown in fig. 2. The Seebeck coefficient is negative at room temperature and as the temperature decreases this value decreases and then a crossover from

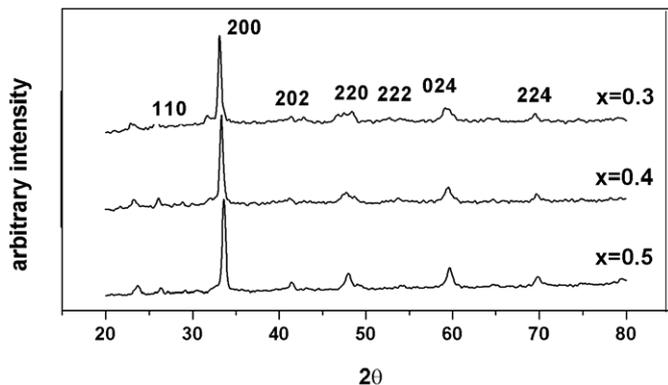


Fig. 1: θ - 2θ XRD pattern of $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$ and 0.5).

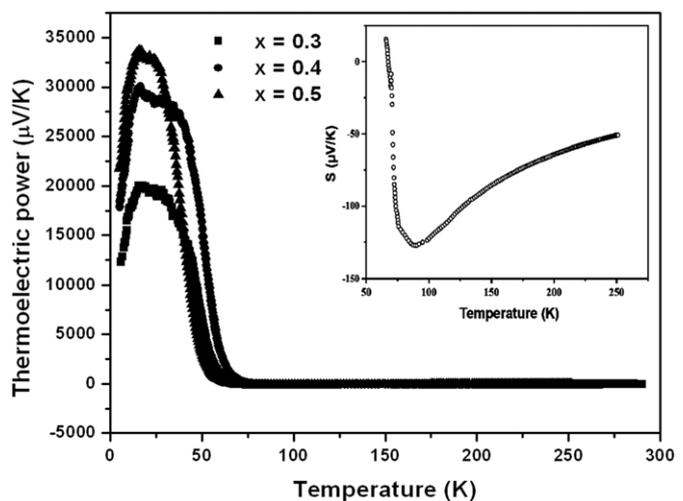


Fig. 2: Variation of thermoelectric power of $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$ and 0.5) with temperature showing a colossal value of the Seebeck coefficient. (The inset shows the zero crossing of thermopower in the case of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.)

negative to positive value occurs at around 70 K. The thermoelectric power sign crossover from negative to positive (as shown in the inset of fig. 2) can be understood if one considers the conduction mechanism in semiconductors. The Seebeck coefficient of a typical semiconductor can be written in the form

$$Q = -\frac{k_B}{e} \left(\frac{\Delta}{k_B T} + B \right). \quad (1)$$

Here Δ is the activation energy which is positive for electrons and negative for holes. B is a constant which is related to the entropy of the carriers [19,20]. Thus it is evident that at temperatures below 70 K, the predominant carriers are holes. It can also be seen that at very low temperatures there is a sharp increase in the thermoelectric power whose onset is at around 70 K and a peak is observed at $\sim 40 \text{ K}$. At this temperature, $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ exhibits a colossal thermoelectric power of 35 mV/K . Coincidentally this is the largest value of thermoelectric power ever reported for these class of materials

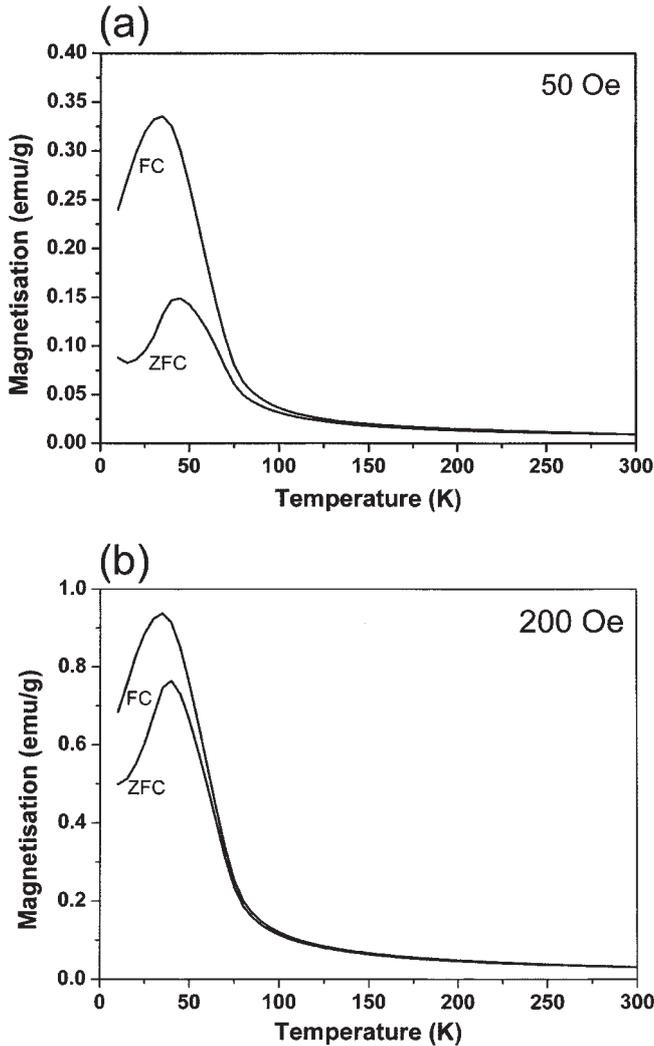


Fig. 3: FC and ZFC magnetisations of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ measured at (a) 50 Oe and (b) 200 Oe.

at this temperature. Colossal thermoelectric power was previously reported for strongly correlated semiconducting FeSb_2 single crystals and reduced TiO_2 single crystals [8,21]. The observance of colossal thermoelectric power in the case of manganites belonging to $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ is here reported for the first time.

The physical origin of such a phenomenon in manganites could be because of various factors. Of the many attributes leading to the exhibition of colossal thermoelectric power namely, phonon drag, magnon drag, charge ordering, spin glass cluster or spin fluctuation, could be contributing individually or collectively to this phenomenon. It was reported that in the case of single-crystal TiO_2 , phonon drag effect of holes contribute to the large positive thermoelectric power [21]. When there exists a temperature gradient, heat flows from a high temperature region to a low temperature region; heat flow can be considered as a flow of phonons and phonon drag is essentially the effect in which carriers are preferentially scattered by the phonons

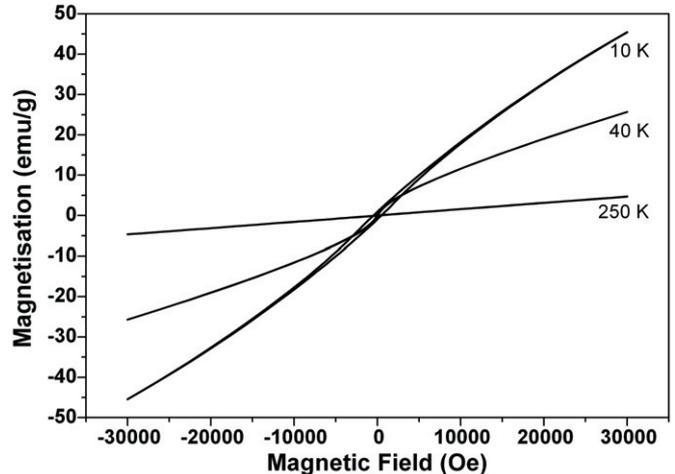


Fig. 4: Magnetisation curves of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ measured at different temperatures.

in the direction of the heat flow. A peak at low temperature has been attributed to the contribution arising out of phonon drag. However in the case of materials exhibiting magnetic ordering, charge carriers are scattered by spin waves and thus magnon drag is also considered responsible for the display of large thermopower at low temperatures.

Since manganites under discussion exhibit magnetic ordering at low temperatures and to get an insight into the phenomenon of colossal thermoelectric power occurring at these temperatures, magnetisation measurements were carried out. Figure 3 is a representative graph showing magnetisation curves, FC and ZFC, for $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ at two different magnetic fields (50 Oe and 200 Oe). The sample shows an irreversible thermomagnetisation process at low temperatures. Under a magnetic field of 50 Oe the splitting between ZFC and FC magnetisation is observed at 125 K and when the field is increased to 200 Oe, the splitting becomes narrower and the splitting temperature (T_{irr}) shifts to 70 K. This splitting is one of the characteristics of spin-glass-like behavior and the shift in the splitting temperature with different magnetic fields is a consequence of the balance between the competing magnetic and thermal energies. These results suggest that this compound is in a spin-glass-like state at temperatures lower than T_{irr} . This spin-glass-like behaviour was already reported in $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ by García-Landa *et al.* [14]. Figure 4 shows the field dependence of magnetisation up to 3 T of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ at different temperatures. It is found that at temperatures lower than T_{irr} (at 10 K and 40 K); the low-field region of magnetisation becomes a nonlinear function of field and also displays hysteresis. This feature is also characteristic of magnetic ordering and is consistent with results of Terai *et al.* [15] on $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. From temperature-dependent magnetisation curves it is evident that a paramagnetic to spin-glass-like transition occurs for the sample under discussion at low temperatures.

It is noteworthy that colossal thermoelectric power of ~ 35 mV/K was displayed at this temperature for the sample $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$ and 0.5). However, studies by other researchers indicate that charge ordering takes place in $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ at temperatures < 90 K [14,16]. Recently, Rhyee *et al.* [22] reported a large figure of merit (~ 1.48) in $\text{In}_4\text{Se}_{3-\delta}$ crystals where in charge density wave instability was attributed to the large anisotropy observed in electric and thermal transport properties. This result suggests that one cannot rule out the contributions of charge ordering to the colossal thermopower. The suggested mechanism is rather tentative and further studies are in progress so as to understand the underlying physics involved in the display of colossal thermoelectric power in these class of compounds.

In conclusion we report a colossal value of Seebeck coefficient for Gd-Sr manganites having the composition $\text{Gd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$ and 0.5) prepared by wet solid-state reaction methods. The samples showed a paramagnetic to spin-glass-like phase transition and it is presumed that the existence of a spin-glass-like state at 40 K is responsible for the large thermoelectric power.

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