Thermopower and nature of the hole-doped states in $LaMnO_3$ and related systems showing giant magnetoresistance

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We have measured the thermopower (S) of hole-doped $LaMnO_3$ systems in order to see its dependence on the Mn^{4+} content as well as to investigate other crucial factors that determine S. We have carried out hole doping (creation of Mn^{4+} by two distinct means, namely, by the substitution of La by divalent cations such as Ca and Sr and by self-doping without aliovalent substitution). The thermopower is sensitive not only to the hole concentration but also to the process employed for hole doping, which we explain as arising from the differences in the nature of the hole-doped states. We also point out a general trend in the dependence of S on hole concentration at high temperatures ($T > T_c$), similar to that found in the normal-state thermopower of the cuprates. [S0163-1829(96)52638-X]

Observation of giant magnetoresistance (GMR) in perovskite oxides of the type $R_{1-x}A_xMnO_3$ (where R = La, Pr, Nd, etc., and A = Ca, Sr, Ba, etc.) has created renewed interest in the structural, magnetic, and electronic transport properties of these materials.[1–11] The electrical transport and magnetic properties depend on the Mn^{4+} content[11] as well as on parameters such as the average A-site cation radius ($\langle r_A \rangle$), here the A site refers to the A site of the perovskite oxide.[9–11] Recent studies[11–15] of thermopower (Seebeck coefficient, S) show that the thermopower can have both signs depending on the temperature and the degree of substitution by the divalent cation (x) which along with the oxygen stoichiometry determine the Mn^{4+} content and hence the resulting carrier concentration. This observation clearly indicates that the carriers are of mixed type (electron and holelike) in these materials.

The Mn^{4+} content (referred to as hole concentration) in these materials can be controlled by two different means: (1) substitution by a divalent cation and (2) by the change in the oxygen stoichiometry. While substitution of La^{3+} by divalent cation increases the Mn^{4+} content, a decrease in oxygen content from the stoichiometry (i.e, oxygen content <3) increases the Mn^{3+} content. Alternatively, creation of cation deficiency (i.e, an increase of the relative oxygen to cation ratio which is occasionally referred to as oxygen excess) also leads to an increase of the Mn^{4+} content. The creation of cation vacancy (both in the La and Mn sites) occurs during the high-temperature annealing of these oxides. We term this latter method to ‘‘self-doping.’’ Thus two samples of manganates can have the same average Mn^{4+} content but can show differences depending on the method of doping which gives rise to the differences in the nature of hole-doped states arising from differences in the microscopic details. This aspect of the nature of the hole-doped states is not qualitatively perceptible in other measurements like magnetization, resistivity, or even magnetoresistance. However, as shown below this difference reveals itself clearly in the Seebeck coefficient S. It is the purpose of this paper to demonstrate that the Mn $^{4+}$ content is not the only factor which determines S and the method of doping also appears to be important leading to qualitative differences.

Samples used in the present study are polycrystalline materials prepared by the sol-gel technique. The ambient of annealing (nitrogen, air, and oxygen) was varied to control the ultimate oxygen stoichiometry (or the relative oxygen-cation ratio). The details of the sample preparation have been given elsewhere.[11,16] All the samples were characterized by x-ray diffraction, resistivity, and ac susceptibility as well as redox titrations for determination of the exact Mn^{4+} content. The Seebeck coefficient (S) was measured by the standard dc technique. We will show that the exact determination of the Mn^{4+} content is extremely important and this will explain the recent conflicting reports[13,14] of thermopower observed in films of these oxides which are mostly uncharacterized as far as the determination of the Mn^{4+} content is concerned.

In Fig. 1 we show the temperature dependence of S for three materials which have the same nominal composition ($La_{0.7}Ca_{0.3}MnO_3$) but differing Mn^{4+} content created by varying the annealing ambient. The materials, annealed at the same temperature (1273 K) for 24 h, have the same average grain size (in excess of 1.5 μm). The as-prepared sample (referred to as sample I) annealed in air has a Mn^{4+} content of 34% implying that it has a higher oxygen-cation ratio (or cation vacancies) since for exact stiochiometry the Mn^{4+} content should be 30%. Sample II, prepared by annealing in nitrogen has 26% Mn^{4+} and a slightly lower oxygen-cation ratio. Sample III, annealed in oxygen under the same condition has 37% Mn^{4+} and hence a large oxygen-cation ratio. In the inset of Fig. 1 we show the resistivities (ρ) and the ac susceptibilities (χ). While the magnitude of ρ changes substantialy by changing the Mn^{4+} content there is relatively little change both in the T_c and the temperature at which ρ shows a maximum (which is

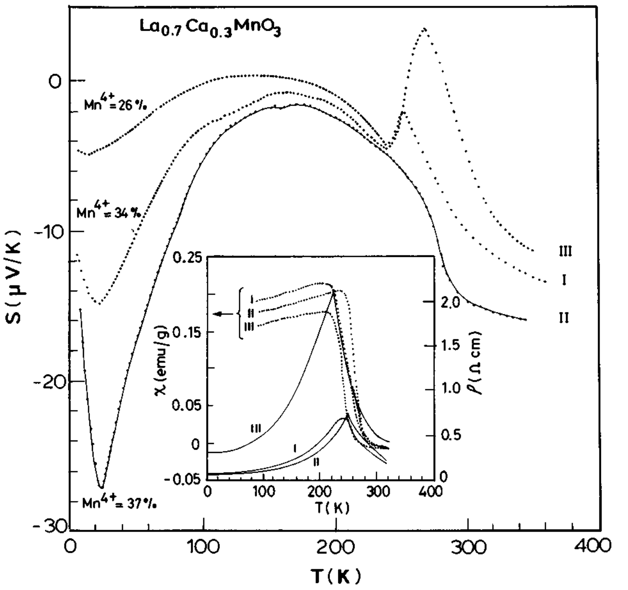

FIG. 1. Thermopower data of $La_{0.7}Ca_{0.3}MnO_3$ samples with varying Mn^{4+} content. The different Mn^{4+} contents are created by varying the annealing ambient. The inset shows the resistivities and the ac susceptibilities.

around 250–270 K). The value of S, however, is extremely sensitive to the Mn^{4+} content and becomes more negative as the Mn^{4+} content is increased. The crossover from positive S to negative S occurs for Mn^{4+} at around 30%. This is in agreement with previous observations[11,12] where hole doping had been carried out by substitution. Thus samples with a similar Mn^{4+} content have qualitatively similar S as long as the the doped states are created predominantly by substitution. (There are a number of contributions which give rise to the rather complex temperature dependence of S. The different contributions which are likely to contribute to S have been discussed before.)[15]

We now consider the samples where the hole doping has been done *only* by ‘‘self-doping.’’ The thermopower data are shown in Fig. 2. Samples IV and V have been prepared with no Ca substitution but by heat treatment and high-temperature oxidation only, which leads to different oxygen-cation ratios and hence different Mn^{4+} content. These samples are not oxygen deficient. On the contrary, the hole doping arises from cation vaccencies created by high-temperature oxidation.[17] The formula of samples IV and V can be written as $La_{0.945}Mn_{0.945}O_3$ and as $La_{0.96}Mn_{0.96}O_3$ respectively. Sample IV (with a cubic structure) has Mn^{4+} content of 33%, similar to sample I ($La_{0.7}Ca_{0.3}MnO_3$). Sample V with Mn^{4+} content of 24% has a rhombohedral structure. The resistivities and the magnetoresistance (MR) of the samples have been reported earlier.[11] The thermopower of the ‘‘self-doped’’ samples are compared with those of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$(marked VI in the inset) with comparable Mn^{4+} contents. The T_c, magnetization, and the MR of samples I and IV are similar and the resistivity shows a similar qualitative behavior (i.e, a peak near T_c) although sample IV has a higher resistivity. What is interesting is that the thermopower of the two self-doped samples (IV and V) are qualitatively different from those of the substitutionally doped samples in spite of similar Mn^{4+} content. This is particularly severe at the lowest temperatures where the self-doped samples show large positive thermopower which increases as T is decreased. Also the peak near the T_c is very prominent for these samples. For sample I the sign of S is negative while it is always positive for samples IV and V. Thus the Mn^{4+} content is not the only factor determining S. This observation is significant and is useful to elucidate the nature of carriers and charge transport in these materials.

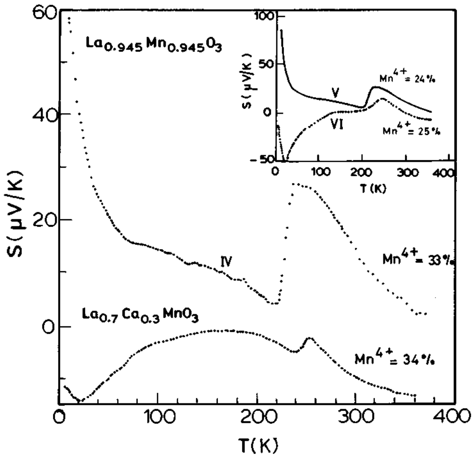

FIG. 2. Thermopower data of self-doped cubic $La_{0.945}Mn_{0.945}O_3$ with 33% Mn^{4+} (marked IV) and $La_{0.7}Ca_{0.3}MnO_3$ with 34% Mn^{4+}. Inset: Thermopower of self-doped rhombohedral $La_{0.96}Mn_{0.96}O_3$ with 24% Mn^{4+} (marked V) and $La_{0.8}Ca_{0.2}MnO_3$ (marked VI) with 24% Mn^{4+}.

The thermopower becomes negative as the Mn^{4+} content increases in $La_{1-x}Ca_xMnO_3$. We want to investigate if the trend continues in the Ca-rich end where the sample loses ferromagnetism and becomes an insulator over the entire temperature range. In Fig. 3, we show S for $La_{0.1}Ca_{0.9}MnO_3$ (with Mn^{4+} content = 86%). S is large and negative. It has a shallow temperature dependence for

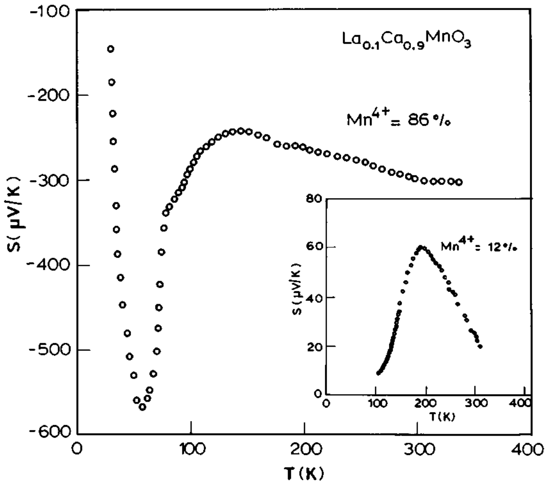

FIG. 3. Thermopower of Ca rich $La_{0.1}Ca_{0.9}MnO_3$ (Mn^{4+}=86%). Inset: Thermopower of self doped $La_{0.98}Mn_{0.98}O_3$ with Mn^{4+} = 12%.

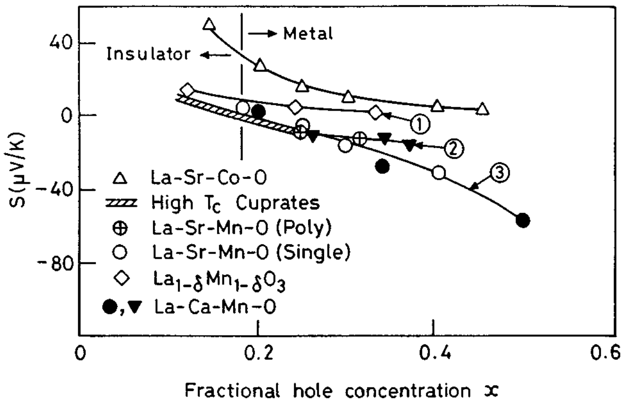

FIG. 4. Thermopower of various oxides systems as a function of fractional hole content x ($x=0.2$ implies 20% Mn^{4+} content). The data on the manganates are from present investigation as well as from Refs. 12 and 15. The data on cuprates (hatched curve) and Co based oxides are from Refs. 18 and 19 respectively.

$T>100$ K with $S(350\text{ K}) \approx -300$ μV/K. It shows a prominent minimum at around 60 K where the value of the thermopower is $\approx$ -600 μV/K. Below 60 K S rises rather sharply as T decreases. We do not understand the origin of this behavior other than the fact that at $T\approx100$ K, the magnetization shows formation of ferromagnetic clusters and the MR shows a peak ($\approx$76% at H = 6 T and at 25 K). At lower temperatures, the temperature dependence of S is similar to that expected of a system with localized charge carriers. The important conclusion is that the sign of the thermopower remains negative when La is doped into $CaMnO_3$ (high Mn^{4+} regime). In the other extreme, for very low Mn^{4+}, these materials are again insulating but the thermopower is positive as shown in the inset of Fig. 3 for the self-doped sample of $LaMnO_3$ with a Mn^{4+} content of 12%. In this regime of hole content, i.e., $Mn^{4+}<25\%$, S is not sensitive to the process of hole doping.

The dependence of S on the hole concentration at high temperatures ($T>T_c$) has a generic aspect as discused below because similar trends have been seen in related materials. We demonstrate this in Fig. 4, where we have plotted the high-temperature thermopower (in the paramagnetic state) for all the samples of the $LaMnO_3$ family. The data have been collected from our experiments (on both Sr and Ca substituted systems) as well as from Ref. 12 (Sr substituted single-crystal systems). For lower hole doping ($Mn^{4+}<25\%$), all the samples show identical dependence of S on the actual Mn^{4+} content (denoted as x in the graph) irrespective of the way the holes are created. However, at higher hole content distinct differences show up. For the ''self- doped'' (curve 1) samples S are always positive and reach almost zero value at high hole concentration. The samples belonging to curve 2 have been created by a combination of substitutional doping and self-doping. The samples belonging to curve 3 have been made mainly by substitutional doping either by Ca or by Sr. The observation shows that there is a systematic trend in the value of S : If the doped hole states are predominantly created by the substitution they have a crossover from positive to negative S as a function of x and the crossover occurs for $x>30\%$. The crossover to negative S is absent for self doped samples. In the same figure we have shown the thermopower of two closely related systems: the high-temperature cuprates and the $La_{1-x}Sr_xCoO_3$ system. It has been shown in Ref. 18 that in a large class of cuprates the thermopower at high temperatures (in the normal state at T = 300 K) has a universal dependence on the hole concentration. We show the data from Ref. 18 in Fig. 4 as a hatched region. This curve matches with the data for our materials very closely. This agreement may be fortuious but the observation that S becomes more negative with increasing hole content is also observed in the high-T_c cuprates. For the $La_{1-x}Sr_xCoO_3$ system[19] also the thermopower shows the same trend. (The Co based system shows a metal insulator transition for $x>0.2$ and a ferromagnetic state for $x>0.18$ with a T_c $\approx$250 K which is due to the creation of Co^{4+}.) It is possible that the observed dependence of S on the hole content is generic in materials with strong hybridization of oxygen p and transition metal d bands with a component of charge transfer between the ligand and the cation.

Recent photoelectron spectroscopic studies[20] have shown the existence of both electron and holelike bands of states respectively below and above the Fermi level which are created by substitution. For the metallic samples the Fermi level lies in the region where these two bands overlap. While the creation of Mn^{4+} in $LaMnO_3$ creates change in the holelike band, creation of Mn^{3+} in $SrMnO_3$ or $CaMnO_3$ fills up the electron doped states. We can then think of charge transport by both type of carriers (i.e, hole and electron) in the Sr and Ca substituted $LaMnO_3$ systems. The observed total thermopower depends on the relative contribution of both type of carriers. The change in the sign of the thermopower as a function of the Mn^{4+} content can thus be thought of as a crossover from a holelike carrier dominated region to an electronlike carrier dominated region.

In contrast to the Ca and Sr substituted systems, the self-doped $LaMnO_3$ has no divalent cation substitution and there are no electronlike states below the Fermi level created by doping. All the carriers are created by filling the doped hole states. As a result this material has only one type of carrier and the thermopower is always positive. We can thus relate the differences in the thermopower S of the two types of materials (self-doped and substitution doped) to the differences in the nature of hole doped states. The important message is that even with the same hole content, the two materials need not have the same nature of the hole doped states if the holes are created by different routes.

The holes created by self-doping are more localized in character. This may be due to strong on-site binding potential for the holes or smaller transfer integral due to relatively larger unit-cell volume (and hence larger Mn-O-Mn distance) or due to large lattice distortion around the missing cations whose absence creates the holes. Increase of S to a large positive value at low temperatures in the self-doped samples can be taken as the sign of onset of hole localization. Similar large thermopower arising from hole localization has also been seen in Y substituted manganates.[21,22] In Y doped samples the localization occurs due to the narrowing of e_g band due to the smaller value of $\langle r_A \rangle$.

In conclusion, we show that the thermopower in the manganates is sensitive to the Mn^{4+} content. But it is not the only determining factor. The nature of hole-doped states in the self-doped samples and the substitutionally doped samples differ substantially even though the samples have the same Mn^{4+} content. This gives rise to qualitative differences in S. These differences are not seen as prominently in other transport properties.

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