The Effects of Heat Treatment on the Electronic Transport of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$

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We report measurements of thermopower and resistivity for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ ceramics treated in different temperatures and atmosphere. Chemical titration is used to determine both of the average valence of manganese and content of oxygen. As the samples are annealed at lower temperatures, the resistivities of both $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ reduce in magnitude. The effect of nitrogen-annealing leads to a reduction of the resistivity for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ but an increase for $La_{0.67}Ca_{0.33}MnO_{3+\delta}$. Thermopower data suggest more than one type of carrier existing in the system. Transport data seem to support the polaron hopping in the high temperature regime.

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I. Introduction

Doped perovskite manganites $La_{1-x}M_xMnO_3$ (M = Ca, Sr, Ba) have recently attracted much attention because of their large magnetoresistance effects [1]. Soon after the discovery, similar effects were found in the layered $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with $x = 0.3$ and 0.4 [2]. The simultaneous onset of ferromagnetism and metal-like conductivity could be qualitatively described by Zener's double exchange mechanism [3]. Millis et al. [4] presented a model, which incorporates the double-exchange mechanism and the polaron formation in the high temperature regime arising from a strong electron-phonon coupling, to explain the observed resistivity behavior and magnetic transition temperature. There are extensive literatures providing evidence of the polaron presence from the magnetic, small angle neutron scattering, and La^{139} NMR experiments [5]. For polaronic transport, the activation energies derived from the measurements of electrical resistivity and thermopower are distinguishable. The electrical conduction for carriers activated to polaronic states can be expressed as

$$\sigma \sim e^{-(E_g+E_p)/2k_BT}, \tag{1}$$

where E_g is the energy gap for carriers being excited across and E_p the polaron binding energy. The thermopower for carriers activated to polaronic states is given by

$$S \sim (k_B/e)(E_g/2k_BT + B), \tag{2}$$

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where B is associated with the spin and the mixing entropy. The activation energy is $E_\rho = (E_g + E_p)/2$ for resistivity measurements, and $E_S = E_g/2$ for thermopower measurements.

Annealing thin films of $La_{1 i x}M_xMnO_3$ at a high temperature of 900 ±C in O_2 was found critical to obtain a large magnetoresistance [1]. In addition, cation vacancy defects were observed in $La_{0.8}Sr_{0.2}MnO_3$ by a high-resolution transmission electron microscopy [6]. A controlled heat treatment in different atmosphere is expected to change the oxygen stoichiometry and valence state of manganese. In this paper, we present temperature dependence of electrical conductivity and thermopower of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ ceramics annealed in flowing oxygen and nitrogen. We find that annealing $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ in nitrogen exhibits the same effects as applying pressure on the behavior of electrical resistivity and thermopower.

II. Experimental

$La_{0.67}Ca_{0.33}MnO_{3+\delta}$ and $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ ceramics were prepared by quantitatively mixing high purity powders of La_2O_3, CaO, $SrCO_3$, and Mn_2O_3. The mixed powders were ground using Retsch Model MM2000 Laboratory Mixer Mill. The thoroughly mixed and ground powders were calcined for 36 hrs with an intermediate grinding. The resulting powders were pressed into rectangular bars and sintered for 18 hrs, followed by annealing at different temperatures in the desired atmosphere for 24 hrs. The heat treatment conditions are summarized in Table I. Powder X-ray diffraction patterns were obtained using a Scintag DMS 2000 X-ray diffractometer equipped with Cu Kα radiation. Resistivity measurements were performed using standard four-probe techniques. Thermoelectric power measurements were performed using steady state techniques. Thermopower data are subtracted from Seebeck probe Cu leads. Iodometric titration was used to determine both of the oxygen content and valence state of manganese.

TABLE I. Heat treatment conditions for synthesizing $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ and $La_{1.4}Sr_{1.6}MnO_{7+\delta}$ ceramics

set	Materials	Calcination Temperature/ Atmospher	Sintering Temperature/ Atmosphere	Annealing Temperature/ Atmosphere	Lattice Constant a	Lattice Constant c	Valence of Mn	δ
A	$La_{0:67}Ca_{0:33}MnO_{3+±}$	1300± C/O_2	1300± C/O_2	950± C/O_2	3.8591(7)		+3.32	-0.005
B	$La_{0:67}Ca_{0:33}MnO_{3+±}$	1300± C/O_2	1300± C/O_2	950± C/N_2	3.8596(7)		+3.31	-0.01
C	$La_{0:67}Ca_{0:33}MnO_{3+±}$	1300± C/O_2	1300± C/O_2	150± C/O_2	3.8623(8)		+3.36	+0.015
D	$La_{0:67}Ca_{0:33}MnO_{3+±}$	1300± C/O_2	1300± C/O_2	150± C/N_2	3.8619(7)		+3.34	+0.005
E	$La_{0:67}Ca_{0:33}MnO_{3+±}$	1300± C/O_2	1300± C/O_2	300± C/vacuum	–	–	–	–
F	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1400± C/air	1500± C/air	950± C/O_2	3.8687(9)	20.157(9)	+3.44	+0.14
G	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1400± C/air	1500± C/air	950± C/air	3.8670(14)	20.203(12)	+3.42	+0.12
H	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1400± C/air	1500± C/air	950± C/N_2	3.8648(7)	20.268(6)	+3.40	+0.10
I	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1490± C/O_2	1500± C/air	800± C/O_2	3.8745(8)	20.132(9)	+3.44	+0.14
J	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1490± C/O_2	1500± C/air	800± C/air	3.8708(11)	20.155(9)	+3.42	+0.12
K	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1490± C/O_2	1500± C/air	800± C/N_2	3.8625(12)	20.258(9)	+3.40	+0.10
L	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1490± C/O_2	1500± C/air	250± C/O_2	3.8754(7)	20.233(8)	+3.48	+0.18
M	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1490± C/O_2	1500± C/air	250± C/N_2	3.8727(8)	20.231(8)	+3.42	+0.12
N	$La_{1:4}Sr_{1:6}Mn_2O_{7+±}$	1490± C/O_2	1500± C/air	300± C/vacuum	–	–	–	–

III. Results and Discussion

All the XRD peaks of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ can be indexed based on a tetragonal and a cubic structure, respectively. As shown in Table I, the variation of lattice constants a and c have an opposite trend for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$. The former decreases with the decreasing partial pressure of oxygen, whereas the latter increases. As a result, the c/a ratio increases with the decreasing partial pressure of oxygen, implying Jahn-Teller distortion is enhanced. In addition, low annealing temperature leads to larger lattice constants and a higher valence of manganese for both $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$.

In comparison with the effects of oxygen-annealing at 800 ±C on resistivity, it is found that nitrogen-annealing leads to a lower resistivity and a higher peak resistivity temperature. The effects of nitrogen-annealing are more prominent in an external magnetic field [7]. Fig. 1 shows the effects of annealing temperature on the electrical resistivity of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ heated in a nitrogen atmosphere. It is found that low annealing temperature tends to reduce the resistivity and leads to a shallow and broad maximum temperature dependence. When the sample is annealed at 300 ±C in an evacuated Pyrex ampoule ($\sim 1.2 \times 10^{i\,5}$ torr), the resistivity is reduced further. The Arrhenius activated conduction is followed in the high temperature regime. The activation energies, E_ρ, are 83 meV, 81 meV, and 17 meV for the annealing temperatures 950 ±C, 800 ±C and 250 ±C, respectively, for samples heated in a nitrogen atmosphere. Fig. 2 shows the effects of annealing atmosphere on the resistivity of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ at the annealing temperature 250 ±C. Similar to the condition of annealing at 800 ±C, nitrogen-annealing results in a reduction of resistivity and a shift of peak resistivity to a higher temperature. According to the model of Millis [4], these results seem to indicate the electron-phonon coupling constant is smaller for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ annealed at a low temperature and a nitrogen atmosphere. Note that electron-phonon coupling constant is related to the phonon stiffness and bandwidth.

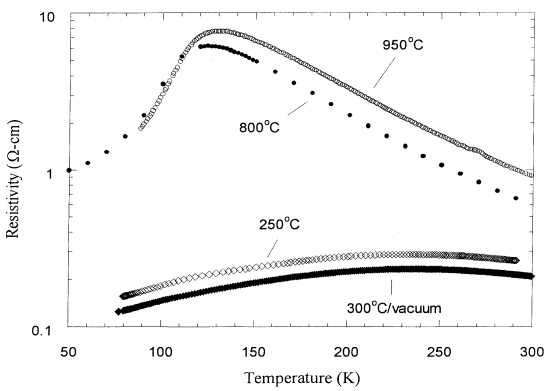

FIG. 1. Temperature dependence of the resistivity for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ annealed at different temperature in a nitrogen atmosphere. The data for the sample annealed in vacuum is shown for comparison.

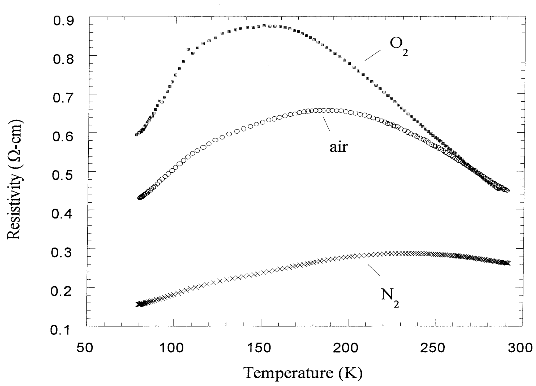

FIG. 2. Temperature dependence of the resistivity for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ annealed at 250 °C in oxygen, air, and nitrogen, respectively.

For $La_{1¡\,x}M_xMnO_{3+\delta}$, a lower Curie temperature is accompanied by a higher peak resistivity and a larger magnetoresistance effect. Fig. 3 shows the effects of annealing temperature on the resistivity of $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ heated in a nitrogen atmosphere. Like $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$, low annealing temperature tends to reduce the resistivity and shifts the peak resistivity to a higher temperature. However, annealing $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ in nitrogen or in an evacuated Pyrex ampoule at 300 ±C shows opposite effects on the electrical resistivity as compared to $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ (inset of Fig. 3). A lower resistivity is obtained as $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ is annealed in oxygen as compared to that annealed in nitrogen. For $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ heated in a nitrogen atmosphere, the activation energies, E_ρ, are 95 meV and 66 meV for the annealing temperatures 950 ±C and 150 ±C, respectively.

Thermopower measurements can give two pieces of information: the type and characteristic energy of charge carriers. Fig. 4 shows the effects of annealing temperature on the thermopower of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ heated in a nitrogen atmosphere. The thermopower for all samples changes its sign twice, suggesting there is more than one type of carriers existing in the system. The difference in thermopower between samples annealed at low temperatures and high temperatures is clearly seen. Low annealing temperature tends to reduce the absolute values of thermopower, which is likely due to the increase of electrical conductivity. For samples heated in nitrogen, the activation energies, E_S, are 6.1 meV, 5.7 meV, and 7.2 meV for the annealing temperatures 950 ±C, 800 ±C and 250 ±C, respectively. As shown in Fig. 5, thermopower behavior is nearly independent of the annealing temperature for $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ in the ferromagnetic state. The rapid drop of the thermopower corresponds to a transition to the metallic state. The larger negative values at high temperatures for the sample annealed at 150 ±C seem difficult to reconcile with the fact that it shows a lower resistivity. The thermopower dependence on the heat treatment in the regime of activated conduction still needs to be clarified. For $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ heated in a nitrogen atmosphere, the activation energies, E_S, are 2.4 meV, and 3.6 meV for the annealing temperatures 950 ±C and 150 ±C, respectively. From the above results, the difference between E_ρ and E_S is clearly seen, which is consistent with the literature [8]. The above data seem to support the polaronic transport in the high temperature regime.

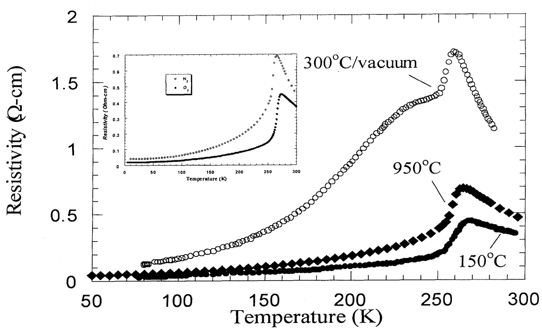

FIG. 3. Temperature dependence of the resistivity for $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ annealed at different temperatures in a nitrogen atmosphere. The inset illustrates that nitrogen annealing results in an increase of the resistivity. The data for the sample annealed in vacuum is shown for comparison.

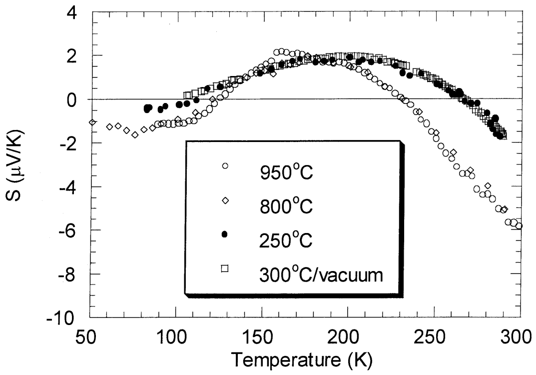

FIG. 4. Temperature dependence of the thermopower for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ annealed at different temperature in a nitrogen atmosphere. The data for the sample annealed in vacuum is shown for comparison.

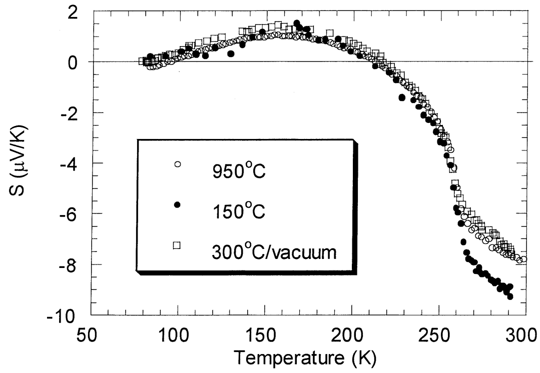

FIG. 5. Temperature dependence of the thermopower for $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ annealed at different temperature in a nitrogen atmosphere. The data for the sample annealed in vacuum is shown for comparison.

IV. Summary

We have measured resistivity and thermopower of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$ heat-treated in different temperatures and atmosphere. Low annealing temperature reduces the resistivity for both $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$. Nitrogen-annealing reduces the resistivity for $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ but increases the resistivity for $La_{0.67}Ca_{0.33}MnO_{3+\delta}$. Thermopower data seem to suggest more than one type of carrier existing in the system. Transport data support the polaronic transport in the high temperature regime. We speculate that the cation defects play a role in the transport properties. The effect of cation defects on the transport properties is left for the future work, which might shed light on the origins of different effects of nitrogen annealing on the resistivity of $La_{1.4}Sr_{1.6}Mn_2O_{7+\delta}$ and $La_{0.67}Ca_{0.33}MnO_{3+\delta}$.

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