Sign Change of Thermopower at Low Temperatures in $Nd_{0.7}(Ca,Sr,Ba)_{0.3}MnO_3$ *

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(Received 22 May 1999)

The temperature dependence of thermopower and resistivity for the series of $Nd_{0.7}(Ca,Sr,Ba)_{0.3}MnO_3$ with a fixed average A-site cation radius $\langle r_A \rangle$ have been measured. Infrared spectra revealed that the size differences between various A-site ions cause large local distortions of MnO_6 octahedra. The thermopower is enhanced above metal-insulator transition temperature T_m and is reduced below T_m by increasing amount of A-site cation disorder. The sign change of thermopower induced by A-site cation disorder has been observed at low temperatures. The observed thermopower behaviors have been explained by Mott's formula and the effect of the spin disorder scattering.

PACS: 72.15.Jf, 71.38.+i, 75.30.Et

The metal-insulator transition is a prominent electrical transport phenomenon in perovskite-type manganese oxides. The transition temperature T_m can be controlled in $L_{1-x}M_xMnO_3$ (L =La, Nd, Pr, Sm; M = Ca, Sr, Ba) by varying the hole-doping x and the average A-site cation radius $\langle r_A \rangle$.[1-3] Application of hydrostatic pressure has a similar effect on T_m.[4-5] Recently Rodriguez and Attfield have pointed out another factor which can control T_m.[6,7] The factor is that the A-site cation disorder can be quantified by the size variance of the A-cation radius distribution $\eta = \langle r_A^2 \rangle - \langle r_A \rangle^2$. They studied the effects of η on T_m, and obtained that T_m shows a strong linear dependence upon η ($dT_m/d\eta = -20600 \pm 500\,K\cdot Å^{-2}$) in a series of the $L_{0.7}M_{0.3}MnO_3$ perovskites with a constant mean A-site cation radius $\langle r_A \rangle = 1.23$ Å. Therefore A-cation disorder with a constant $\langle r_A \rangle$ shows interesting effects and should be investigated further.

In this paper, we present the measurements of the IR spectra, resistivity and thermoelectric power to demonstrate this A-cation disorder effect. We have prepared a series of six samples $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$ (Table 1) in which η is systematically varied by using different compositions of Ca, Sr and Ba. These samples are designed to have a fixed rare earth element (Nd), a fixed doping level ($x = 0.3$) and a fixed mean A-site radius ($\langle r_A \rangle = 1.21$ Å, calculated from tabulated values[8]) in order to insure that the observed changes are mainly caused by A-site cation disorder. It is found that the symmetry of MnO_6 octahedron reduces as η increasing and that the A-site cation disorder can induce sign change of thermopower at low temperatures.

The samples were prepared from stoichiometic amounts of Nd_2O_3, MnO_2, $CaCO_3$, $SrCO_3$, and $BaCO_3$ by solid state reaction under identical conditions. After pre-sintered with three intermediate grindings in air at 1000−1200°C for three days, the mixtures were then pressed into pellets and sintered at 1420°C for 16 h. In order to minimize micro-inhomogeneity, the sintered hard pellets were broken to pieces, reground to fine powder, and again pressed into pellets. The final sintering was carried out in air at 1440°C for 12 h. The samples were then slowly cooled down to room temperature. X-ray powder diffraction (XRD) patterns indicate that the obtained samples are of clear single phase with Pnma space group. Electrical resistivity was measured by the standard four-probe method. The measurements of IR transmission spectra (Nicolet 700) are carried out on powder samples in which KBr is used as a carrier. The IR spectra taken are in the frequency range from 4000 to 350 cm^{-1}. The thermoelectric power measurements were performed in a cryostat working from 300 K down to liquid nitrogen temperature.

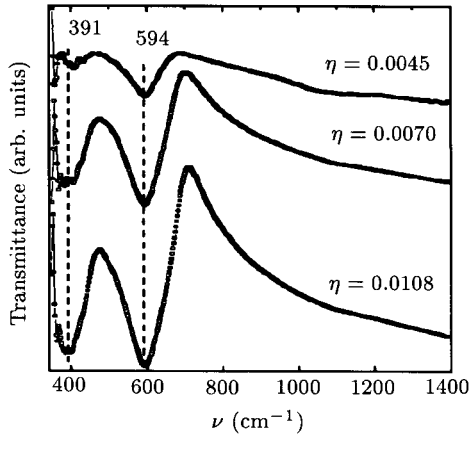


Fig. 1. Infrared transmittance spectra for $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$ with $\eta = 0.0045, 0.0070$, and 0.0108 Å^2, at room temperature, respectively.

*Supported by the Foundation of the Chinese Academy of Sciences under Grant No. KJ951-A1-401, and the Science Foundation of Anhui Province, China.

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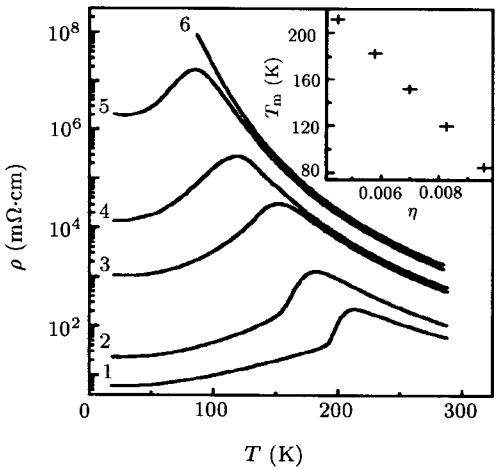


Fig. 2. Temperature dependence of resistivity for $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$ with different variance η. The samples are numbered in order of increasing η.

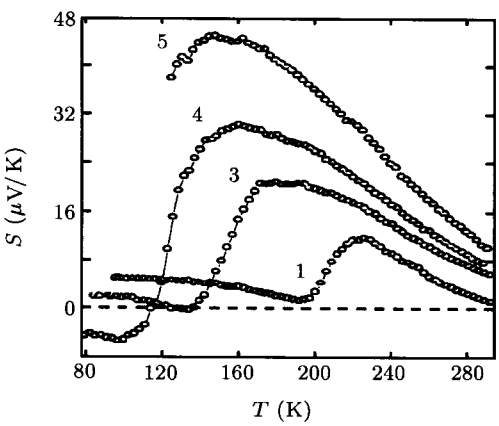


Fig. 3. Thermopower vs temperature for nominal $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$ series. For clarity, the curves for the samples numbered with 2 and 6 are not plotted.

A-site cation disorder results mainly in random displacements of oxygen atoms from their average crystallographic positions.[6,7] This can be evidenced directly by IR spectra which are sensitive to local lattice distortions. Figure 1 depicts the observed IR spectra of the three mixed oxides with $\eta = 0.0045$, 0.0070, and 0.0108 Å^2, respectively. Obviously, two strong absorption regions are present for all samples. One is the negative peaks around $\nu = 594\,\mathrm{cm}^{-1}$ assigned to the stretching vibration mode of the MnO_6 octahedron in which the Mn-O bond distance is modulated; another is the negative peaks around $\nu = 391\,\mathrm{cm}^{-1}$, the bending vibration in which the Mn-O-Mn bond angle is modulated.[9] As seen in Fig. 1, the bending vibration becomes more prominent with increasing η, which directly reflects that the symmetry of the local MnO_6 octahedra reduces with increasing η due to random displacements of oxide ions. Therefore it can be stated that A-cation disorder leads to local distortions of MnO_6 octahedron which can be viewed as the random impurity potential in the lattice.

The temperature dependence of resistivity at zero-field for the six samples, which are numbered in order of increasing η, is shown in Fig. 2. The striking feature observed here (the inset to Fig. 2) is that T_m shows a strong linear dependence on η. A similar phenomenon was also observed and intensively studied by Rodriguez and Attfield[6,7] in $L_{0.7}M_{0.3}MnO_3$ with $\langle r_A \rangle = 1.23$ Å. In Fig. 2, it is clear that the resistivity increases with increasing η (for fixed temperature). Note that for $\eta = 0.0108$ Å^2, ρ increases sharply with decreasing temperature and exceeds the experimental limit.

Figure 3 shows the temperature dependence of thermopower for the samples. Each sample showed a positive enhancement of $S(T)$ as the temperature was lowered to T_m. When $\eta \geq 0.0096$ Å^2, thermopower for samples 5 and 6 becomes unmeasurable at temperatures below about 120 K where most of the mobile holes have become trapped. The resistivity of these two samples was greater than 10^6 mΩ·cm below 120 K, which makes the open-circuit-like noise greater than the signal. Moreover, the maximum thermopower increases with increasing η. In the other four samples ($\eta < 0.0096$ Å^2), the thermoelectric power decreases as increasing η at lowest temperatures (for fixed temperature). Near the resistive transition temperature T_m, the thermopower collapses from large values at higher temperatures to lower values, which shows more characteristic of metallic conduction.

We highlight two features: (1) Figs. 2 and 3 demonstrate that increasing η accompanied by increasing ρ correlates with decreasing S at the low temperatures (say 100 K). On the contrary, increasing η accompanied by increasing ρ correlates with increasing S at the high temperatures (say 280 K). (2) Sign change of thermopower induced by η has been observed at low temperatures. Considering that all the samples with the same doping levels, the same mean radius $\langle r_A \rangle$ and the same trivalent A-cation, the sign change and the observed change regularities of thermopower should be attributed mainly to the effect of cation disorder in A-site.

The increase in $\rho(T)$ with decreasing temperature above T_m can be viewed as a result of increasing trapping of mobile charge carriers.[10] Consequently, within a semiconductor-like picture, thermopower is expected to increase when $T > T_m$. Similarly, at a fixed temperature above T_m, say 280 K, the increase of the resistivity with increasing η can be interpreted as resulting from a reduced carrier mobility due to local distortions of MnO_6 octahedron caused by A-cation disorder. Consequently, thermopower is also expected to increase with the increase of η.

Mott's formula[11]

$$S = (-\pi^2/3)(k_B^2 T/e)[\sigma'(E_F)/\sigma(E_F)]$$

may help to explain the thermopower behaviors below

T_m, where k_B is Boltzmann's constant, e the elementary charge, and $\sigma(E_F)$ the conductivity at Fermi level. On cooling through T_m, the one-electron bandwidth suddenly increases accompanied by insulator-metal transition,[2] which suggests a weak energy dependence on conductivity ($\sigma' \approx$ const).[12] Therefore, according to Mott's formula, thermopower should sharply decrease and become small value similar to metallic features. At fixed temperature below T_m (say 100 K), the sign change induced by η cannot be interpreted simply by Mott's formula alone. Asamitsu *et al.*[12] argued that if the degenerate of the e_g band was lifted for some reason in ferromagnetic phase, the sign change of S could occur. But to the series of $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$, the observed sign change at low temperatures is not from the increase of e_g degenerate degree due to the same divalent doping level.

It has been observed just below T_m in $La_{0.75}Sr_{0.25}MnO_3$ and $La_{2/3}Ca_{1/3}MnO_3$ systems[12,13] that thermopower increases with decreasing spin disorder scattering by use of an applied magnetic field. Therefore it can be expected that increasing the degree of spin disorder can decrease thermopower and cause sign change at low temperatures. In the case of increasing η in the cation disorder system of $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$, the observations that ρ increases sharply in ferromagnetic phase are due to the decreasing mobility of carriers, therefore according to the double exchange theory the increase of η should result in the gradual loosening of collinearity of the overall magnetic order. Consequently, it can be expected for a fixed temperature below T_m in $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$ that the spin disorder scattering increases with increasing η, which should be responsible for the observed sign change of thermopower (see Fig. 3). On the other hand, it is observed that the temperature dependence of thermopower shows a minimum below T_m while thermopower begins to increase again as temperature further decreases (see Fig. 3), such thermopower behaviors also confirm the effects of spin disorder scattering, because it is known that the spin disorder scattering decreases with the lowering of temperature at ferromagnetic state.

According to the present study and the literature[1-7] we know that T_m depends on hole doping x, A-site mean radius $\langle r_A \rangle$, application of hydrostatic pressure and A-site variance η. Thermopower is also affected by these factors. To our knowledge, literature revealed so far that thermopower decreases systematically with increasing hole doping x (Ref. 12) or with increasing A-site mean radius $\langle r_A \rangle$ (Ref. 14) or with increasing application of hydrostatic pressure[5] in the whole observed temperature range (approximately from 0 to 300 K). However, according to the present study it was shown that thermopower increases above T_m and decreases below T_m as η increases. Such a unique effect of η on thermopower should be noted, and detailed temperature dependence of the low-temperature thermopower deserves further investigation.

Table 1. Cation-size variance η, resistivity maximum ρ_m, and the metal-insulator transition temperature T_m measured from resistivity for a series of $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$ with constant $\langle r_A \rangle = 1.21$ Å.

Sample	η (Å^2)	ρ_m (Ω·cm)	T_m (K)
1 $Nd_{0.7}Sr_{0.3}MnO_3$	0.0045	0.226	211
2 $Nd_{0.7}Ca_{0.033}Sr_{0.24}Ba_{0.027}MnO_3$	0.0058	1.321	182
3 $Nd_{0.7}Ca_{0.066}Sr_{0.18}Ba_{0.054}MnO_3$	0.0070	31.334	152
4 $Nd_{0.7}Ca_{0.099}Sr_{0.12}Ba_{0.081}MnO_3$	0.0083	285.190	119
5 $Nd_{0.7}Ca_{0.132}Sr_{0.06}Ba_{0.108}MnO_3$	0.0096	17447.300	84
6 $Nd_{0.7}Ca_{0.165}Ba_{0.135}MnO_3$	0.0108	—	—

In summary, the IR spectra measurements confirm that increasing A-cation size variance η results in increasing local distortions of MnO_6 octahedra in orthomanganites $Nd_{0.7}(Ca, Sr, Ba)_{0.3}MnO_3$ with a constant average A-cation radius $\langle r_A \rangle = 1.21$ Å. Such local structure distortions can be viewed as the random impurity potential, greatly increase resistivity and decrease metal-insulator transition temperature. T_m shows strong linear dependence on η which is consistent with the results obtained by Rodriguez and Attfield.[6,7] Temperature dependence of thermopower has been measured and the sign change induced by A-cation disorder has been observed at low temperatures. We argued that the sign change of thermopower should be attributed to the effect of the spin disorder scattering.

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