



ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Solid State Chemistry 172 (2003) 1–5

JOURNAL OF
SOLID STATE
CHEMISTRY

<http://elsevier.com/locate/jssc>

High-temperature thermopower and conductivity of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ($0.02 \leq x \leq 0.35$)

V.L. Kozhevnikov,^{a,*} I.A. Leonidov,^a E.B. Mitberg,^a M.V. Patrakeev,^a Y.M. Baikov,^b
V.S. Zakhvalinskii,^c and E. Lähderanta^d

^a Ural Division of Russian Academy of Science, Institute of Solid State Chemistry, GSP 145 91 Pervomaiaskaia, Ekaterinburg 620219, Russia

^b Physico-Technical Institute, RAS, St.-Petersburg 194021, Russia

^c Institute for Applied Physics, Academy of Sciences of Moldova, Kishinev 2028, Moldova

^d Wihuri Physical Laboratory, University of Turku, Turku 20014, Finland

Received 12 September 2002; accepted 18 December 2002

Abstract

Thermopower and conductivity are measured for the perovskite-like manganite $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ($0.02 \leq x \leq 0.35$) in the temperature range 200–950°C and oxygen pressure varying between 10^{-11} and 0.5 atm. The data for thermopower and electrical conductivity indicate a transport mechanism dominated by adiabatic hops of small polarons. The high-temperature limit for the thermopower is mainly defined by the spin contribution while configurational contribution does not depend essentially on the doping level. Changes in the conductivity with doping are shown to reflect variations in the mobility of charge carriers.

© 2003 Elsevier Science (USA). All rights reserved.

Keywords: Lanthanum–barium manganite; Thermopower; Electrical conductivity; Small polarons, Charge carrier mobility

1. Introduction

There is a general consent that properties of the acceptor doped, perovskite-like manganites stem from an interaction between the spin, charge and lattice degrees of freedom. Their interplay leads to a polaron-like transport both in the low temperature metal and in the high-temperature insulator-like states. However, the nature of charge carriers is still a controversial issue. Laiho et al. [1] argue for spin polarons. Mizusaki et al. [2] suggest a small lattice polaron type conductivity while Poulsen [3] arrives to conclusion that both small and large polaron models are equally applicable to manganites. It is necessary to notice that discussions of high-temperature transport features are often based only on the defect chemistry consideration and analysis of the equilibrium oxygen content [3,4] when it is difficult to decide whether the conductivity variations with doping may be driven by changes in the carrier density or the mobility. The manganites doped with calcium or strontium attract most intense research

efforts [3]. On the other hand, substitution of barium for lanthanum may be of interest also because the tolerance factor increases faster at the doping. Therefore, one can expect stronger changes in the crystalline lattice at smaller variations of the dopant content, i.e. larger sensitivity of properties, particularly conductivity, to changes in the doping level. In order to gain insight into the nature of the transport mechanism, we have performed thermopower measurements on Ba-doped lanthanum manganite ceramic samples over a wide range of concentrations, temperatures and partial pressures of oxygen in addition to the basic characterization by electrical conductivity measurements. In contrast to electrical conductivity, thermopower depends mainly on concentration of charge carriers and thus is relatively insensitive to changes in their mobility or to the influence of grain boundaries. We will show that for this material the high-temperature thermopower is consistent with small polaron carriers hopping in paramagnetic state. The magnitude of thermopower shows that there are considerably more carriers per transport site than would follow from a nominal valence consideration. Independently on the doping level, the thermopower is found to contain mainly the spin

*Corresponding author. Fax: +007-3432-744-495.

E-mail address: kozhevnikov@imp.uran.ru (V.L. Kozhevnikov).

contribution. Hence, conductivity changes with barium content follow changes in mobility, which are caused by deformations in the crystal lattice.

2. Experimental

The samples $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ($x = 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.25, 0.30$ and 0.35) used in this study were prepared by a conventional solid-state reaction method. Starting materials were oxides La_2O_3 (99.99%), Mn_2O_3 (99.5%) and barium carbonate BaCO_3 (99.94%). The raw materials were pre-calcined to remove adsorbates, weighed in desirable amounts and thoroughly mixed with a mortar and pestle with addition of ethanol. The mixtures were pressed into pellets and fired at 900–1300°C in air. The materials were crushed into powder, pressed and fired several times with gradually increasing the temperature before single-phase specimens were obtained. Control of phase purity and determination of crystal lattice parameters were carried out with X-ray diffraction ($\lambda = 1.54178 \text{ \AA}$). Room temperature lattice parameters for the obtained samples were found in close agreement with data in work [5].

The synthesized samples were ball milled and pressed into discs under 2 kbar uniaxial load. The disks were sintered at 1450°C to a density of about 95% of theoretical. Rectangular bars $2 \times 2 \times 18 \text{ mm}^3$ were cut from the sintered pellets for electrical measurements. One specimen, equipped with butt electrodes and thermocouples, was used for measurements of thermopower α . The temperature gradient in the furnace along the sample was about 15 K/cm. Another specimen was used in four-probe measurements of the d.c. conductivity σ . Current leads of platinum wire (0.3 mm) were tightly wound to the sample at 16 mm spacing while the spacing between the potential probes was 10 mm. The specimen was placed perpendicular to the specimen for thermopower measurements so that the temperature gradient along the sample was zero. The measurements of conductivity and thermopower were carried out simultaneously in a cell utilizing oxygen sensing and pumping properties of cubically stabilized zirconia oxygen electrolyte as described elsewhere [6]. The cell was filled with a 50% O_2 , 50% CO_2 gas mixture in the beginning of the experiment and sealed. A typical value of the pump current necessary to maintain a desirable oxygen pressure $p\text{O}_2$ inside the cell did not exceed 0.5 mA. The electrical parameters were measured with a high-precision Solartron 7081 voltmeter. Experimental data points were collected only after equilibrium had been achieved between the sample and ambient oxygen gas, that is when changes in the logarithm of the conductivity did not exceed 0.01% per minute and changes in thermopower did not exceed $0.001 \mu\text{V}/\text{min}$.

The measurements were carried out in isothermal runs. The measurements were halted upon achievement of the desirable low-pressure limit. Then the oxygen pressure was increased to the starting upper limit where measurements were repeated in order to confirm reversibility of the experiment; thereupon temperature was changed thus enabling the next measuring cycle. Thermopower data were corrected for the contribution of the platinum leads [7].

3. Results and discussion

Fig. 1 shows the thermopower and conductivity versus the logarithm of the oxygen partial pressure at 950°C in specimens with different barium content. The thermopower increases when the pressure decreases from $p\text{O}_2 = 0.5 \cdot 10^{-5} \text{ atm}$ in the sample with $x = 0.02$ and, then, remains practically invariable at further decrease of the pressure down to 10^{-11} atm . The transition from the pressure dependent to the pressure independent behavior occurs at higher pressures when barium content is larger and above $x \geq 0.20$ thermopower becomes pressure independent in the entire measured pressure range. This behavior is in agreement with the well-known robustness of manganites. For instance, a small oxygen excess is observable at 1000°C in samples slightly doped with strontium only at pressures above 10^{-3} atm while oxygen deficiency

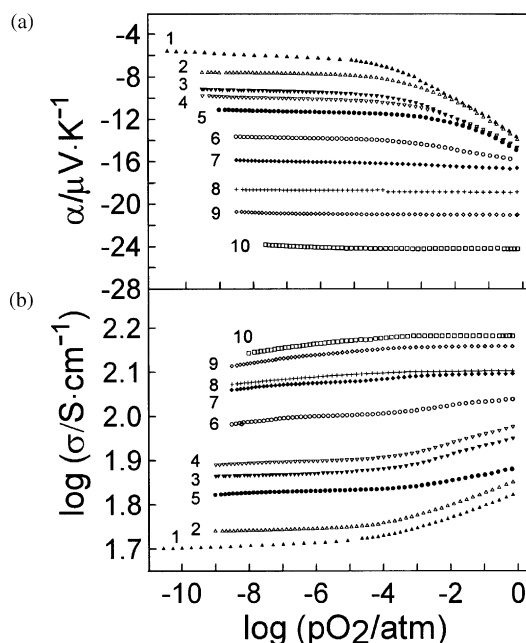


Fig. 1. The pressure dependence of the thermopower (a) and of the logarithm of the conductivity (b) in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ with different doping $x = 0.02$ (1), 0.04 (2), 0.06 (3), 0.08 (4), 0.10 (5), 0.15 (6), 0.20 (7), 0.25 (8), 0.30 (9), 0.35 (10). The temperature of the experiment is 950°C.

appears when the pressure is smaller than 10^{-12} atm [3]. The insensitivity of thermopower to variations of the oxygen pressure in a wide range reflects invariable oxygen content in the manganites. This is a valuable feature because changes in properties are not obscured by variations in the carrier concentration due to the red-ox equilibrium of the manganites with the surrounding gas phase oxygen. Fig. 2 shows the thermopower dependence on barium content at 950°C under different oxygen pressures. The downward bent of the isobar at $p\text{O}_2 = 0.21$ atm does not reflect an intrinsic feature but is rather related to a shift of the solid–gas equilibrium with a change in the acceptor content. At the same time, thermopower varies practically linearly with barium doping at 10^{-6} atm when changes in the concentration of the carriers are driven only by internal processes in the solid. Remarkably, the thermopower sign is negative in the high-temperature range as seen in Figs. 1 and 2. This sign is consistent with apparent electronlike transport. However, electron holes are known to be dominant charge carriers in the acceptor doped perovskite-like manganites [2–4]. The negative sign can be explained by a temperature dependent term, which increases with temperature and, thus, results in a change of the sign from positive to negative at high temperatures. This is seen in Fig. 3 where the thermopower tends to positive values with decreasing the temperature. Similar behavior is observed also at doping with calcium or strontium [8,9]. Thermopower changes practically linearly with inverse temperature (solid lines in Fig. 3), and only above approximately 800°C deviations are observed from the linearity, which are caused by the solid–gas equilibrium. Thus, when oxygen content in the elementary unit is constant, the temperature dependence of thermopower in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ may be approximated by the equation

$$\alpha = \frac{k}{e} \left(\frac{\varepsilon_x}{T} \right) + \alpha_\infty, \quad (1)$$

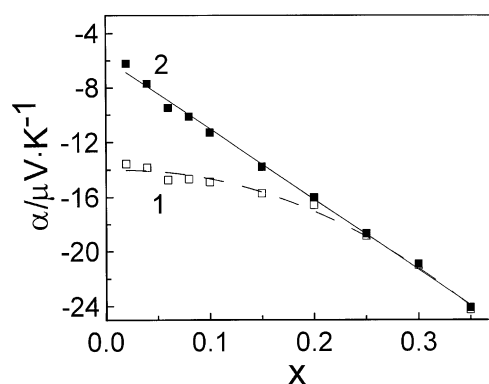


Fig. 2. The thermopower in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ versus barium doping. The partial oxygen pressure is $p\text{O}_2 = 0.21$ (1) and 10^{-6} atm (2) and the temperature of the experiment is 950°C .

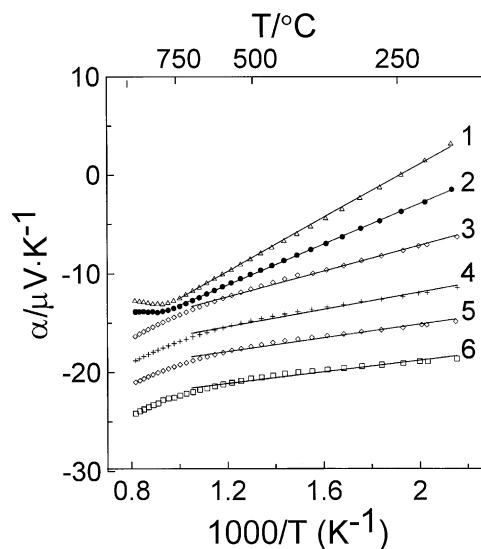


Fig. 3. The thermopower versus inverse temperature for the samples of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ with different barium content $x = 0.04$ (1), 0.1 (2), 0.20 (3), 0.25 (4), 0.3 (5), 0.35 (6). The oxygen pressure is 0.21 atm. Lines show fittings to Eq. (1).

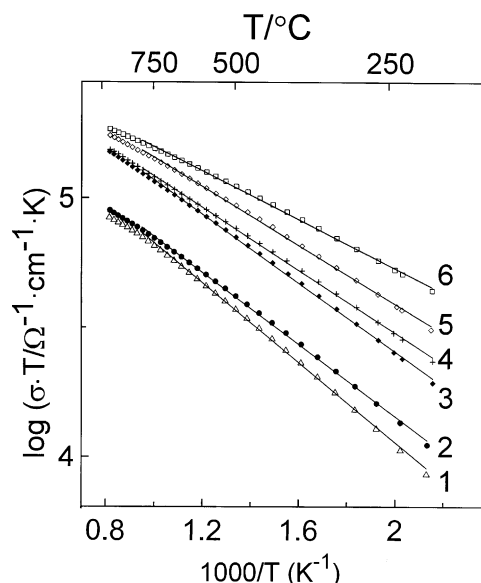


Fig. 4. The logarithm of the conductivity versus inverse temperature for the samples of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ with different barium content $x = 0.04$ (1), 0.1 (2), 0.20 (3), 0.25 (4), 0.3 (5), 0.35 (6). The oxygen pressure is 0.21 atm. Lines show fittings to Eq. (2).

where k and e are the Boltzmann constant and absolute value of the electron charge, respectively, while ε_x and α_∞ are material parameters. The parameter ε_x is positive as it must be for hole conduction. Fig. 4 shows the conductivity at $p\text{O}_2 = 0.21$ atm. Up to 800°C it can be described by

$$\sigma = \frac{\sigma^\circ}{T} \exp\left(-\frac{\varepsilon_\sigma}{T}\right), \quad (2)$$

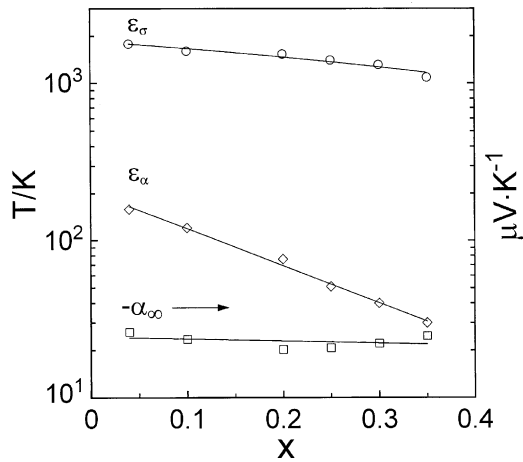


Fig. 5. The conductivity and thermopower parameters versus barium content in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$.

where σ° and ε_σ are constants. Fig. 5 shows the variations of the parameters ε_α , α_∞ and ε_σ with barium content obtained from the linear fittings of the plots in Figs. 3 and 4. The activated nature of Eqs. (1) and (2) and the large difference between parameters ε_α and ε_σ suggest that high-temperature transport in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ occurs via adiabatic hops of small polarons [10].

It is seen from Fig. 5 that the parameter ε_α decreases with the increase of barium content within the studied range of the doping. When extrapolated to larger barium contents this parameter tends to a small, nearly zero value almost exactly at $x = 0.5$. In a semiconductor this may take place when the conduction band becomes half-filled. In manganites the conduction band is associated mainly with $\text{Mn}^{3+}(e_g)$ states [11], and it is only one quarter filled near $x = 0.5$. One may suggest a splitting of this band by some distortion. This is not possible because the structure tends to decrease distortions from cubic symmetry with the increase in barium content [5]. Moreover, even in the case of the splitting it would be very improbable for contributions from the resulting bands to cancel each other so perfectly well and, at the same time, to preserve the simple activated behavior of thermopower at large variations of doping and temperature. Physical meaning of the parameter ε_α in polaronic conductors is often associated with the energy difference between identical lattice distortions with and without the carrier. More precisely, the respective contribution originates from the interaction of polarons [12] with each other or with other, e.g. spin, excitations. Therefore, the value of ε_α gives the energy scale for the possible interactions. The increase in the doping results to a state where interaction (scattering) of polaron carriers is so small that they jump over available sites almost like free particles, i.e. this state may bear metal-like properties. In difference with this extreme,

when doping is moderate the polaron carriers cannot be approximated as non-interacting particles. It is quite possible that these interactions may have a relation to the development of transport and magnetic properties at lower temperatures in manganites with $x \approx 0.1-0.3$ [1,11].

When temperature is high and the energy contribution can be neglected, the thermopower approaches the temperature independent term α_∞ , which can be interpreted as configuration entropy per carrier [13]. For the high-spin holes Mn^{4+} ($S = 3/2$) jumping over a network of high-spin Mn^{3+} ($S = 2$) ions, the thermopower may be expressed as

$$\alpha_\infty = \frac{k}{e} \ln \left(\frac{1}{\beta} \frac{1 - c_p}{c_p} \right), \quad (3)$$

where c_p is fractional hole concentration and $\beta = 5/4$ is the degeneracy factor. From this relation one can expect a strong dependence of α_∞ from the doping level. However, it follows from the experimental data in Fig. 5 that α_∞ depends only weakly on the doping. The average value of $\alpha_\infty \approx -23 \mu\text{V/K}$ is close to the spin contribution $(k/e) \ln(1/\beta) = 86 \ln(4/5) = -19 \mu\text{V/K}$ in Eq. (3). It is known that charge disproportionation may provide carriers in manganese oxides [9]. The Mn^{3+} and Mn^{4+} ions, relevant to the hole transport, are present in the manganites in the amounts $1 - x - 2\xi$ and $x + \xi$, respectively. The disproportionation parameter, ξ , may generally depend on doping and temperature. Hence, the fractional concentration of holes can be calculated as $c_p = (x + \xi)/(1 - \xi)$. In order to have a weakly x -dependent fractional hole concentration near $1/2$, according to Eq. (3) and experimental data for α_∞ in Fig. 5 the disproportionation parameter must decrease nearly linearly from $\xi \approx 0.3$ at $x = 0.02$ to $\xi \approx 0.1$ at $x = 0.35$. The unusual feature of this result is that the configurational contribution to the thermopower is very small. This may occur when this term is at minimum with respect to variations in the number of charge carriers, i.e. at charge ordering. Another opportunity may take place when the configurational contribution is at maximum as it can happen at phase separation of the manganate in microscopic regions with $x = 0$ and 0.5 .

We have neglected the possibility of formation of the vacancies on the (La, Ba) sublattice. Such vacancies are known to appear at high oxygen pressures [3]. Nonetheless, one may suppose existence of the quenched vacancies in the samples under study. The respective change in the concentration of holes can be easily calculated [1]. If such vacancies are taken into account in any reasonable amount it does not result in a viable modification in x -dependence of the disproportionation parameter thus leaving the configurational contribution unaffected. Fig. 6 shows the x -dependence of the conductivity at 950°C and $p\text{O}_2 = 10^{-6}$ atm. It follows from the suggested analysis of the thermopower that the

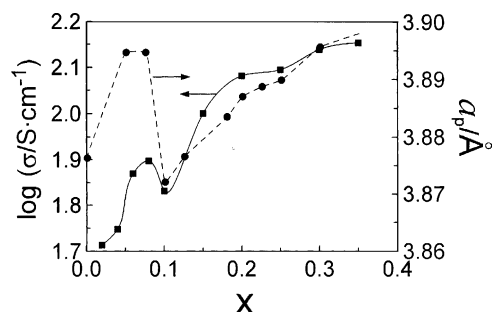


Fig. 6. The logarithm of the conductivity versus barium content in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ at 950°C and $p\text{O}_2 = 10^{-6}$ atm (solid line). The dashed line shows respective changes in the pseudo-cubic lattice parameter according to the data from work [5].

amount of hole carriers in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ does not depend essentially on x in the studied range. Therefore, the irregular increase in the conductivity with x reflects mainly the changes in the mobility of hole carriers because of the deformations in the crystal lattice. This can be seen also from comparison of the conductivity and reduced lattice parameters [5].

More traditional interpretation of the high-temperature thermopower in manganites is known where the energy contribution in Eq. (1) is neglected and only the configurational term, Eq. (3), is taken into account [8,9]. The temperature dependence of the thermopower is thus believed to originate solely from variations of the fractional concentration c_p that in turn are driven by temperature changes of the disproportionation parameter. This approach is not always consistent because calculations at a constant temperature of the disproportionation parameter in such a picture often result in the increase of ξ with x in apparent controversy with the equilibrium consideration.

4. Conclusions

Thermopower and conductivity are measured for $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ at different doping, temperature and oxygen pressure. It is shown that the high-temperature electron transport mechanism involves jumps of small polarons. It is not quite clear from the obtained data

whether the carriers are magnetic or lattice polarons though variations of mobility that follow changes in the lattice parameters may suggest lattice polarons involving distortions of the manganese–oxygen octahedra. It is shown that the polarons cannot be considered as quasi-free particles. The typical scale for the interaction energy is about 10^2 K at moderate doping. The high-temperature limit for the thermopower is consistent with hopes of positively charged mobile particles having spin $3/2$ over a rigid network of sites having spin 2. The independence of the high-temperature thermopower on the doping level suggests an ordered nature of the carriers in the manganites.

Acknowledgment

The support of this work by the INTAS under the grant # 2000-00728 is gratefully appreciated.

References

- [1] R. Laiho, K.G. Lisunov, E. Lähderanta, P. Petrenko, V.N. Stamov, V.S. Zakhvalinskii, *J. Magn. Magn. Mater.* 213 (2000) 271–277.
- [2] J. Mizusaki, Y. Yonemura, H. Kamata, K. Ohyama, N. Mori, H. Takai, H. Tagawa, M. Dokiya, K. Naraya, T. Sasamoto, H. Inaba, T. Hashimoto, *Solid State Ionics* 132 (2000) 167–180.
- [3] F.W. Poulsen, *Solid State Ionics* 129 (2000) 145–162.
- [4] J. Nowotny, M. Rekas, *J. Am. Ceram. Soc.* 81 (1998) 67–80.
- [5] V.A. Cherepanov, E.A. Filonova, V.I. Voronin, I.F. Berger, *J. Solid State Chem.* 153 (2000) 205–211.
- [6] E.B. Mitberg, M.V. Patrakeev, A.A. Lakhin, I.A. Leonidov, V.L. Kozhevnikov, K.R. Poepplmeier, *J. Alloys Comps.* 274 (1998) 103–109.
- [7] N. Cusack, P. Kendall, *Proc. Phys. Soc.* 72 (1958) 898–901.
- [8] E.O. Ahlgren, F.W. Poulsen, *Solid State Ionics* 86–88 (1996) 1173–1178.
- [9] J.W. Stevenson, M.M. Nasrallah, H.U. Anderson, D.M. Sparlin, *J. Solid State Chem.* 102 (1993) 175–184.
- [10] A.J. Bosman, H.J. Van Daal, *Adv. Phys.* 19 (1970) 1–117.
- [11] B. Dabrowski, X. Xiong, Z. Bukowski, R. Dybziński, P.W. Klamut, J.E. Siewenie, O. Chmaissem, J. Shaffer, C.W. Kimball, J.D. Jorgensen, S. Short, *Phys. Rev. B* 60 (1999) 7006–7017.
- [12] D.B. Marsh, P.E. Parris, *Phys. Rev. B* 54 (1996) 16602–16607.
- [13] J.-P. Doumerc, *J. Solid State Chem.* 110 (1994) 419–420.