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Phase separation and insulator–metal behaviour in highly Ba^{2+}-doped $La_{1-x}Ba_xMnO_3$ compounds

S L Yuan, C S Xiong, Z Y Li, Z C Xia, G Q Zhang, G Peng, F Tu, Y P Yang, J Liu, L Liu and Y H Xiong

Institute of Materials Physics and Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

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Abstract

Investigations of structural and transport features of $La_{1-x}Ba_xMnO_3$ with $x = 1/3$ and $2/3$ are performed. The $x = 2/3$ sample is shown to be phase separated into a mixture of $La_{2/3}Ba_{1/3}MnO_3$ and $BaMnO_3$ with the same volume fractions, ∼50%. In this two-phase system, $La_{2/3}Ba_{1/3}MnO_3$ regions are connected in a percolative manner, so the electrical transport is dominated by flow along these percolative paths. Using the recently proposed random resistor network based on electronic phase separation between ferromagnetic metallic and paramagnetic insulating domains, we show that the model can yield results in quantitative agreement with the resistance versus temperature dependence measured for the $x = 1/3$ and $2/3$ samples by using the metallic number density as a fitting parameter. This approach suggests a simple quantitative picture that can be used to explain the insulator–metal behaviour in $La_{1-x}Ba_xMnO_3$ with higher x.

Doped manganese oxides of the form $R_{1-x}A_xMnO_3$ (R is a rare-earth ion and A is a divalent ion such as a Ca, Sr, Ba, or Pb ion) have stimulated considerable scientific and technological interest because of their exotic magnetic and electronic properties [1][1]. Most notable of these properties are the insulator–metal (I–M) behaviour and the colossal magnetoresistance (CMR). Recent studies suggest that these properties tend to be related to intrinsic inhomogeneities due to the presence of strong tendencies toward phase separation (PS) [2][2], typically including (1) electronic PS between two different phases that leads to nanometre-scale coexisting clusters and (2) disorder-induced PS that can induce up to micrometre-scale coexisting clusters driven by disorder near the first-order I–M transitions. Experiments on $La_{0.7}Ca_{0.3}MnO_3$ near T_C have indeed indicated the existence of nanometre-scale ferromagnetic metallic (FMM) domains within the paramagnetic insulating (PMI) matrix [3, 4]. Experiments on $La_{5/8-y}Pr_yCa_{3/8}MnO_3$, on the other hand, showed the coexistence of micrometre-scale FMM and charge-ordered insulating (COI) domains at low temperatures [5].

[1] For a review of the manganites, see [1].
[2] For a review of phase separation, see [2].

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Based on the PS between metallic and insulating domains, two phenomenological approaches to the resistivity of manganites have been proposed by Mayr *et al* [6] and Yuan *et al* [7]. In the approach proposed by Mayr *et al* [6], the authors used the Monte Carlo method to mimic the complicated fractal-like structure in which metallic filaments with resistance $R_M^{\rm per}$ are connected in parallel with insulating portions with resistance R_I. To yield results in agreement with experiments on manganites, the following assumptions are made in their approach: (i) $R_M^{\rm per} \ll R_I$ at low temperatures; (ii) $R_M^{\rm per} \sim R_I$ at intermediate temperatures; and (iii) $R_M^{\rm per} \gg R_I$ at high temperatures. This approach is shown to be appropriate for describing the electrical transport in those manganites, like $La_{5/8-y}Pr_yCa_{3/8}MnO_3$, in which giant FMM and COI domains coexist. In contrast to this, the approach proposed by Yuan *et al* [7] is based on the existence of FMM domains within the PMI matrix, and assumes that FMM particles (with number density p which is a function of temperature and magnetic field) and PMI particles randomly occupy the nodes of a network lattice which is realized through the Monte Carlo method. Using $p(T, H)$ as only fitting parameter whose behaviour is similar to the experimental curve of magnetization, it is found that this approach can yield results in quantitative agreement with experiments on $R_{2/3}A_{1/3}MnO_3$ (for instance, $(La_{0.8}Y_{0.2})_{2/3}Ca_{1/3}MnO_3$ ($T_C \sim 87$ K), $La_{2/3}Ca_{1/3}MnO_3$ ($T_C \sim 250$ K) [7] and $La_{2/3}Ba_{1/3}MnO_3$ ($T_C \sim 335$ K) (the present work)). These compounds have tolerance factors ranging between 0.91 and 0.95 and hence cover the whole range in which only PMI and FMM regions are present in the phase diagram [8] of temperature versus tolerance factor developed for $R_{1-x}A_xMnO_3$ ($x \sim 0.3$).

In addition to the intrinsic PS mentioned above, it is also likely that some manganese perovskites will undergo a different PS into a mixture of two phases with different crystalline structures, which is normally accomplished through the atomic diffusion due to the chemically driven inhomogeneity. This is a conventional structural phase separation (SPS) and is not intrinsic to manganites. Because it is not intrinsic to manganites, the SPS as a physical problem has been less studied for manganites. However, the occurrence of the SPS strongly affects the physical properties of manganites; therefore, it is also important for the correct understanding of manganese physics. In this respect, $La_{1-x}Ba_xMnO_3$ may provide a prototypical example. Earlier measurements of x-ray diffraction (XRD) by and the micro-Raman spectrum of $La_{1-x}Ba_xMnO_3$ revealed that the perovskite structure is stable for $x \leqslant 0.35$ while the SPS occurs for $x > 0.35$ [9–11]. This is different from the case for $La_{1-x}Ca_xMnO_3$, in which the perovskite structure is stable for the whole composition range [13]. This difference leads to different observations of physical properties in the two systems. In particular, $La_{1-x}Ba_xMnO_3$ is ferromagnetic at low temperatures and shows I–M behaviour even for x as high as 0.75 [11, 12]. The purpose of the present work is to provide a possible scenario for the interpretation of the electrical transport observed in $La_{1-x}Ba_xMnO_3$ with higher x, based on our analysis of crystalline structure, transport behaviour and Monte Carlo simulation of the resistance versus temperature dependence using the phenomenological model [7] proposed recently.

Two samples with typical compositions, $La_{2/3}Ba_{1/3}MnO_3$ and $La_{1/3}Ba_{2/3}MnO_3$, were used in the present study; these were fabricated by the conventional solid-state reaction method. Stoichiometric amounts of the starting materials La_2O_3, $BaCO_3$ and $MnCO_3$ were mixed thoroughly and calcined at ~1000 °C for 24 h. The powder thus obtained was ground, pelletized and sintered at ~1300 °C for 24 h, with one intermediate grinding, and then furnace cooled to room temperature.

The structural characterization was done by means of XRD at room temperature with Cu Kα radiation. Shown in figure 1 are XRD patterns for both samples. The $x = 1/3$ sample, as indicated in figure 1(a), crystallizes in a single phase, showing the characteristic peaks of the perovskite structure similar to those previously reported [10] for similar compositions.

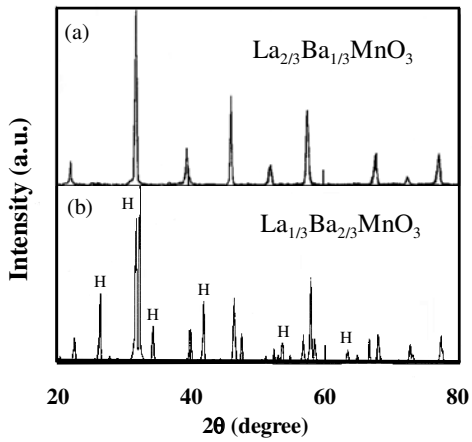

Figure 1. The XRD pattern measured for $La_{1-x}Ba_xMnO_3$ with $x = 1/3$ (a) and $2/3$ (b). The XRD peaks from the hexagonal phase are marked by 'H'.

For the $x = 2/3$ sample, as shown in figure 1(b), the XRD peaks are composed of diffraction peaks from the perovskite structure and some additional XRD peaks marked by H. According to earlier studies on similar compounds [9,10], these additional XRD peaks are due to the presence of hexagonal $BaMnO_3$. This implies that $La_{1/3}Ba_{2/3}MnO_3$ is phase separated into a mixture of $La_{2/3}Ba_{1/3}MnO_3$ perovskite and $BaMnO_3$ hexagonal phase. For the sake of discussion, we consider the more general case in which $La_{1-x}Ba_xMnO_3$ with $x \geqslant 1/3$ is separated into $La_{2/3}Ba_{1/3}MnO_3$ and $BaMnO_3$, i.e., $La_{1-x}Ba_xMnO_3 \rightarrow (1-y)La_{2/3}Ba_{1/3}MnO_3 + yBaMnO_3$, where $y = \frac{1}{2}(3x - 1)$ and $1 - y = \frac{3}{2}(1 - x)$ are the volume fractions of $BaMnO_3$ and $La_{2/3}Ba_{1/3}MnO_3$, respectively. Systematic investigations on $La_{1-x}Ba_xMnO_3$ show that SPS occurs as x exceeds $1/3$ and the volume fraction of the hexagonal phase increases with further increasing x [9, 10, 12]. For the present special composition (i.e., $x = 2/3$), the two phases have close volume fractions, ∼50%. This can be confirmed from the XRD patterns, in which the relative intensities of the XRD peak near $2\theta = 30^\circ$ for the two phases are close.

The electrical transport is studied experimentally by measuring resistivity as a function of temperature by means of the standard four-probe method. The results are shown in figure 2 for both samples. The $x = 1/3$ sample shows thermally activated insulating-like behaviour at high temperatures, with resistivity rising on cooling. After the resistivity passes through a maximum at $T_p \sim 330$ K, further cooling brings about a sharp reduction in it, indicating metallic behaviour. For the $x = 2/3$ sample, we also observe the transition to a metallic state; however, the transition becomes smooth and moves towards a lower-temperature region as compared with the $x = 1/3$ sample. We also note that, compared with the $x = 1/3$ sample, both the peak value and the low-temperature resistivity are clearly increased for the $x = 2/3$ sample. Systematic investigations on $La_{1-x}Ba_xMnO_3$ indicate that the behaviour observed for the $x = 2/3$ sample seems to be a property common to samples with x between 0.5 and 0.75 [12]. As x exceeds 0.75, the sample shows typical insulating behaviour over the whole temperature range. It is interesting to note that, except for different magnitudes of resistivity, the temperature dependences of the resistivity are almost identical for samples with x between 0.5 and 0.75 [12].

On the basis of the SPS found from the XRD, a possible scenario for the interpretation of the experimental observations mentioned above is as follows. $BaMnO_3$ is insulating over the whole temperature range studied. $La_{2/3}Ba_{1/3}MnO_3$, on the other hand, is PMI above T_C,

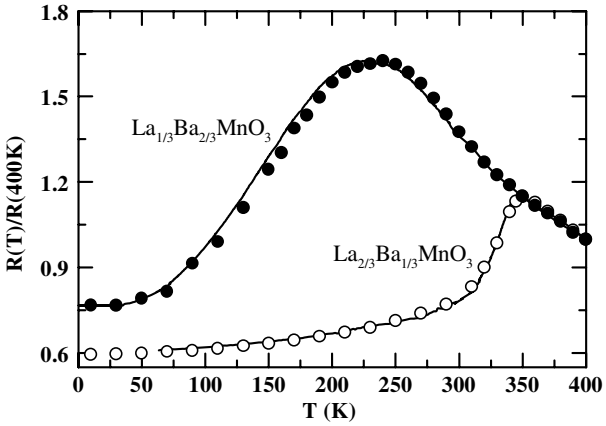

Figure 2. Temperature dependences of the resistance for $La_{1-x}Ba_xMnO_3$ with $x = 1/3$ and $2/3$, where the resistance is normalized by the resistance value at $T = 400$ K. The solid curves are experimental curves and the symbols represent simulated data (see the text).

but its room temperature resistivity ($\sim 10^{-2}$ Ω cm) is larger at least by four orders than that of $BaMnO_3$ [12]. It is therefore reasonable to argue that $La_{1/3}Ba_{2/3}MnO_3$ is a two-phase system consisting of a conducting phase, $La_{2/3}Ba_{1/3}MnO_3$, and an insulating phase, $BaMnO_3$, having the same volume fraction, $\sim 50\%$. Since the conductor fraction is larger than the percolation threshold ($\sim 30\%$ for three dimensions [14]), we expect the conductor regions to be connected in a percolative manner, which is schematically illustrated by the dark area in figure 3(a). The total sample resistance can then be obtained by considering a simple system of two parallel resistances, as indicated in figure 3(b), where $R^{\rm per}$ and R^I are the resistances of the percolative paths (dark area in figure 3(a)) from the conducting phase $La_{2/3}Ba_{1/3}MnO_3$ and of the paths (white area in figure 3(a)) from the insulating phase $BaMnO_3$, respectively. Since $R^I \gg R^{\rm per}$, current can flow actually only along the percolative paths. This means that the transport behaviour in $La_{1/3}Ba_{2/3}MnO_3$ is actually dominated by $La_{2/3}Ba_{1/3}MnO_3$. This suggests a simple qualitative picture that can be used to visualize why the resistivity in this compound has the peculiar shape it has. Similar reasoning is also appropriate for the other samples with higher x—for instance, $x = 0.75$. For this composition, the volume fraction of conductors is simply estimated to be $\sim 37.5\%$, which is still larger than the percolation threshold, so its transport behaviour is dominated by the percolative $La_{2/3}Ba_{1/3}MnO_3$ paths. This suggests a simple interpretation of previous experimental observations [12] that indicate resistance dependences on temperature that are almost the same for samples with $x = 0.63$ and 0.75. Our interpretation can be also supported by the following experimental fact: the disappearance of I–M behaviour in $La_{1-x}Ba_xMnO_3$ as x exceeds a value which is empirically found to be between 0.75 and 0.88 [12]. In the present case, using 30% (the percolation threshold) as the value of the conductor fraction below which the conducting regions are disconnected from each other, we can then infer that as $x \geqslant 0.8$, the sample becomes insulating over the whole temperature range. This is in good agreement with previous experiments [12].

From the above discussion, we know that the transport in $La_{1/3}Ba_{2/3}MnO_3$ is actually dominated by $La_{2/3}Ba_{1/3}MnO_3$ conductors which are connected in a percolative manner. As shown in figure 2, however, the I–M behaviour in the $x = 2/3$ sample is clearly different from that of the $x = 1/3$ sample, suggesting that the effect caused by the presence of the insulating $BaMnO_3$ phase in $La_{1/3}Ba_{2/3}MnO_3$ still needs to be considered. This can be understood from the following approach to the temperature dependences of the resistance measured for the

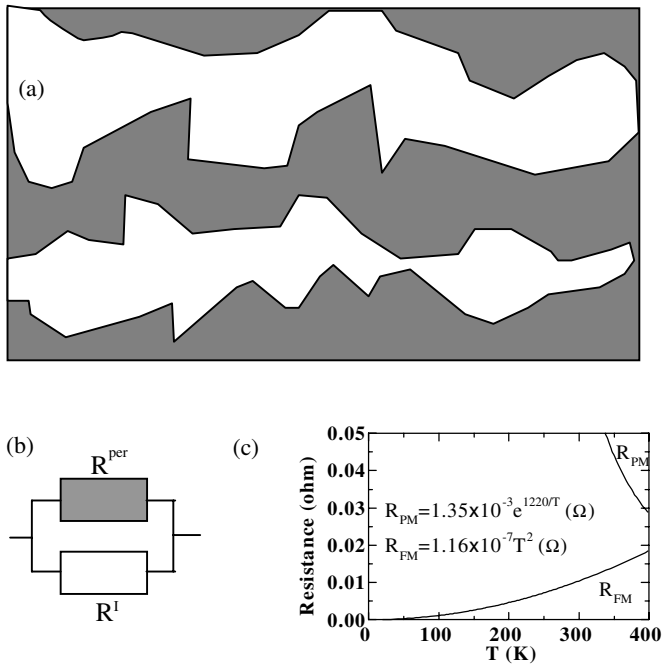

Figure 3. (a) A schematic illustration of the SPS between conducting $La_{2/3}Ba_{1/3}MnO_3$ regions (dark area) and insulating $BaMnO_3$ regions (white area). (b) The two-resistance model for the situation indicated in (a). (c) Temperature dependences of R_{PM} and R_{FM} used in the simulation (see the text).

two samples using the recently proposed random-resistor-network model [7] based on the electronic PS between PMI and FMM domains.

The physical basis and main assumptions for the random-resistor-network model proposed in [7] are summarized here.

(1) The sample is phase separated near T_C into a mixture of FMM and PMI domains.
(2) These domains are modelled as particles that randomly occupy the nodes of a network lattice.
(3) The kind of particle residing at the ith node depends on the value of a computer-generated random number. If this number is smaller than the chosen p-value, this node is assigned a FMM particle; otherwise it is assigned a PMI particle. Here p is the number density of FMM particles.
(4) Current is conducted through a 'bond resistance' R_{ij} between two adjacent nodes. As two adjacent nodes are occupied by FMM (or PMI) particles, R_{ij} is determined as $R_{ij} = R_{FM}$ (or R_{PM}), where R_{FM} (R_{PM}) is the resistance of the individual FMM (PMI) particles; while as two adjacent nodes are occupied by particles of different kinds, R_{ij} is determined by $R_{ij}^{-1} = R_{PM}^{-1} + R_{FM}^{-1}$.

Through this process, the random resistor network is constructed and the sample resistance is then obtained by solving the Kirchhoff equations using a simple iterative procedure.

Three quantities, R_{FM}, R_{PM} and p, are involved in the above-mentioned model. For a pure $La_{2/3}Ba_{1/3}MnO_3$ sample, R_{PM} and R_{FM} can be directly extracted from the resistance versus temperature dependences measured at $T \gg T_C$ and $T \ll T_C$, respectively. The thus-obtained

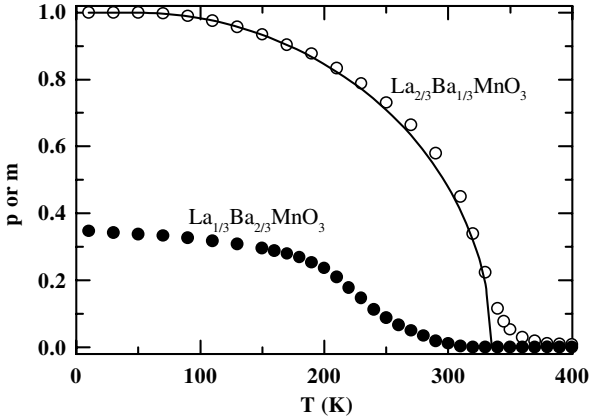

Figure 4. Temperature dependences of the number density of FMM particles, $p(T)$, used in the simulation of $R(T)$ for $La_{1-x}Ba_xMnO_3$ with $x = 1/3$ (open circles) and $2/3$ (solid circles). The reduced magnetization m (solid curve) as a function of temperature is also plotted for comparison.

R_{PM} and R_{FM}, as functions of temperature, are plotted in figure 3(c). Because p is the number density of FMM particles, it should be proportional to the volume fraction of FM phase and hence to the spontaneous magnetization M_s. It is therefore reasonable to consider $p(T)$ as $p(T) = M_s(T)/M^{\text{sat}}$, where M^{sat} is the saturation magnetization corresponding to the full ordered moment of Mn ions. Assuming the sample to be of high quality, it is then expected that the sample will show robust FM behaviour at low temperatures, implying that $M_s(T) \to M^{\text{sat}}$ or $p(T) \to 100\%$ as $T \to 0$ K. Near or above T_C, as revealed in experiments [15], there is a tail on the magnetization versus temperature curve which can extend up a temperature much higher than T_C. In view of this fact, we have actually assumed $p(T)$ to be as indicated by the open circles in figure 4; it is used as a fitting parameter for the simulation of the R versus T dependence for the pure $La_{2/3}Ba_{1/3}MnO_3$ sample. For comparison, in figure 4 we also plot the reduced magnetization $m(T)$ (solid curve) calculated from the mean-field self-consistency equation [16]

$$m = B_J\left(\frac{3J}{J+1}\frac{m}{t}\right) \tag{1}$$

with $J = 1.83$ and $T_C = 335$ K, where B_J is the Brillouin function and $t = T/T_C$ is the reduced temperature. It can be found that, except for the temperature range near T_C, no difference exists between the two sets of curves, $p(T)$ and $m(T)$. Using the thus-obtained R_{PM}, R_{FM} and p, we can obtain a simulation curve for the resistance versus temperature dependence. The simulated results (open circles) as indicated in figure 2 show excellent agreement with experimental data (solid curve) measured for $La_{2/3}Ba_{1/3}MnO_3$.

A similar simulation can also be performed for the resistance versus temperature dependence measured for $La_{1/3}Ba_{2/3}MnO_3$. The results are displayed by solid circles in figure 2, together with the corresponding experimental data (solid curve); these show excellent agreement. In this simulation, we keep both R_{PM} and R_{FM} the same as for pure $La_{2/3}Ba_{1/3}MnO_3$, but use p-values (as indicated by solid circles in figure 4) as fitting parameters to yield results in agreement with experimental data. As discussed above, the transport in $La_{1/3}Ba_{2/3}MnO_3$ is along the percolative $La_{2/3}Ba_{1/3}MnO_3$ paths. Therefore, it is reasonable for R_{PM} and R_{FM} to be the same for the two samples. One notes that for $La_{1/3}Ba_{2/3}MnO_3$, as compared with $La_{2/3}Ba_{1/3}MnO_3$, $p(T)$ is substantially decreased over the whole temperature

range below T_C and the maximum value of p is only $\sim$0.35. This can be understood if one notes the following two facts.

(1) As discussed above, $La_{1/3}Ba_{2/3}MnO_3$ contains $\sim$50% $La_{2/3}Ba_{1/3}MnO_3$; therefore, the maximum value of p is only 0.5 even assuming that all Mn spins in this 50% $La_{2/3}Ba_{1/3}MnO_3$ are ferromagnetically ordered.
(2) The presence of $BaMnO_3$ phase would affect the FM alignment of Mn spins in $La_{2/3}Ba_{1/3}MnO_3$, thus causing further decrease in p.

In summary, we have investigated both the structural and electrical transport features of $La_{1-x}Ba_xMnO_3$ with $x = 1/3$ and $2/3$. On the basis of our approach, we propose the possibility of the existence of two kinds of phase separation in $La_{1-x}Ba_xMnO_3$ with higher x. One is between conducting $La_{2/3}Ba_{1/3}MnO_3$ and insulating $BaMnO_3$ regions; this is a normal SPS and is not intrinsic in nature. As the volume fraction of conducting $La_{2/3}Ba_{1/3}MnO_3$ is above the percolation threshold, the electrical transport in $La_{1-x}Ba_xMnO_3$ is dominated by the percolative $La_{2/3}Ba_{1/3}MnO_3$ paths. The other kind is between FMM and PMI regions; this occurs among the percolative $La_{2/3}Ba_{1/3}MnO_3$ paths and is intrinsic to manganites. We therefore believe that $La_{1-x}Ba_xMnO_3$ is to be regarded as a prototypical compound when studying the PS problem.

Acknowledgments

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