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Influence of Oxygen Stoichiometry on Electrical Transport and Magnetic Properties of Doped Perovskite-type Ferrate and Manganate Single Crystals

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Abstract

The electrical transport and magnetic properties of $(La_{1-x}Sr_x)FeO_{3-\delta}$ *and* $(La_{1-x}Sr_x)MnO_{3-\delta}$ *single crystals were studied as a function of the dopant concentration* x *and the oxygen deficiency* δ. *Crystals were grown by the floating zone process and subjected to post-annealing treatments in oxidizing or reducing atmosphere to control* δ. *This two-step process allows the precise control of* δ. *Moreover, a wide range of* δ *values not attainable by changing only the growth conditions can thus be studied. Controlling the Fe and Mn valencies via the oxygen deficiency was found to affect the magnetic and electrical properties profoundly. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Perovskites containing lanthanides (Ln) and transition metal (TM) oxides with 3*d* electron orbitals may exhibit various electric and magnetic phenomena such as metal–insulator (M–I) transitions, antiferromagnetic (AF) and ferromagnetic (F) ordering, and charge (C) ordering. Among these materials, the ferrate $(La_{1-x}Sr_x)FeO_{3-\delta}$ and manganate $(La_{1-x}Sr_x)MnO_{3-\delta}$ systems, where the average valency v of the Mn or Fe transition metal varies between +3 and +4, have attracted considerable interest.

The electrical and magnetic behavior in the $(La_{1-x}Sr_x)FeO_{3-\delta}$ system is affected by both AF and C ordering. The AF Néel temperatures (T_N) of the stoichiometric ($\delta = 0$) $(La_{1-x}Sr_x)FeO_3$ subsystem range from 750 K ($x=0$, $LaFeO_3$) to 135 K ($x=1$, $SrFeO_3$).[1] Compounds with low x values are semiconducting, with the resistivity decreasing with increasing x up to about $x=0{\cdot}5$. At high x, samples are metallic at high temperature, but M–I transitions occur upon cooling due to AF and C ordering.[2,3] $SrFeO_3$ ($x=1$) is metallic down to 4 K. Two other subsystems studied are $(La_{1-x}Sr_x)FeO_{3-\delta}$ with Fe completely reduced to Fe^{3+} ($\delta = x/2$) and oxygen-deficient strontium ferrate ($x=1$) $SrFeO_{3-\delta}$. Compounds with only Fe^{3+} are insulating, for specific La:Sr ratios tend to show intergrowth of perovskite $LaFeO_3$ and brownmillerite $SrFeO_{2{\cdot}5}$, and have very high values of T_N between 700 K ($SrFeO_{2{\cdot}5}$) and 750 K ($LaFeO_3$).[3] $SrFeO_{3-\delta}$ undergoes phase separation due to ordering of oxygen vacancies into $SrFeO_{2{\cdot}50}$, $SrFeO_{2{\cdot}68-2{\cdot}73}$, $SrFeO_{2{\cdot}86}$ and $SrFeO_{2{\cdot}97-3{\cdot}00}$, which typically occurs between 1100 and 500 K.[2]

The $(La_{1-x}Sr_x)MnO_{3-\delta}$ system exhibits magnetic ordering at low temperatures, which strongly influences its resistivity.[4] $LaMnO_{3-\delta}$ ($x=0$) is an AF insulator below $T_N=150$ K. Increasing x gives rise to an F insulator ($0{\cdot}08<x<0{\cdot}16$) and F metal for $0{\cdot}16<x<0{\cdot}6$. Owing to the high stability of the Mn^{4+} ion, samples are oxygen hyperstoichiometric ($\delta < 0$) for $x<0{\cdot}4$ and stoichiometric ($\delta = 0$) for $x>0{\cdot}4$ under ambient oxygen pressure.[5] This leads to some uncertainty in the value of δ for $x<0{\cdot}4$. The aim of this work is to examine the effect of combined doping and oxygen deficiency (or excess) on the electric and magnetic properties of single crystals of the aforementioned ferrate and manganate systems.

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2 Experimental

All crystals were grown by the floating zone method in air except $SrFeO_{3-\delta}$, which was grown in Ar as this was found to minimize cracking problems. The $x = 0{\cdot}8$ ferrate samples were not single crystalline, and exhibited cracking. Nevertheless, the properties of the resulting fragments could be measured. To reduce inhomogeneities, these samples were annealed for 1 day at 1400°C in O_2. The oxygen deficiency δ in the ferrates was controlled by equilibration at different temperatures and oxygen pressures according to thermogravimetric studies, followed by quenching to room temperature. 'Oxidized' samples for $x > 0{\cdot}5$ were annealed at 500°C in high pressure (10 MPa) O_2, which yielded δ values of 0·00 ($x = 0{\cdot}5$), 0·01 ($x = 0{\cdot}8$) and 0·03 ($x = 1{\cdot}0$). Three sets of samples resulted, which we denote as (A) oxidized $(La_{1-x}Sr_x)FeO_{3-\delta}$ ($\delta \ll x$) with x as a parameter, (B) reduced $SrFeO_{3-\delta}$ and (C) reduced $(La_{0\cdot2}Sr_{0\cdot8})FeO_{3-\delta}$, with δ as a parameter. Small pieces as-grown in air of the manganate crystals were oxidized by heating them to 500°C in 100 kPa O_2 for 1–2 days. Reduction required a procedure different from the ferrates because of the stability of Mn^{4+}. These samples were first equilibrated in a thermobalance (Setaram) at 1000°C in 2 kPa O_2, then slowly reduced by injecting dilute H_2 gas and simultaneously monitoring the weight change. The achieved δ was confirmed by reoxidizing part of the sample in the thermobalance. These thermal treatments also result in three sets of samples, which we denote as (D) as-prepared, (E) oxidized $(La_{1-x}Sr_x)MnO_{3-\delta}$ ($\delta < 0$ for $x < 0{\cdot}4$ and $\delta = 0$ for $x \geq 0{\cdot}4$), with x as a parameter ($0 \leq x \leq 0{\cdot}6$), and (F) reduced $(La_{0\cdot4}Sr_{0\cdot6})MnO_{3-\delta}$, with δ as a parameter ($\delta \geq 0$). Powder X-ray diffraction (XRD) was used to determine the phases and lattice parameters. The electrical resistivity was measured on crystal pieces with a four-wire method with In or silver paint contacts. The orientation of the crystals for magnetic and electrical measurements was random.

3 Results and Discussion

3.1 Ferrates

Figure 1 shows the electrical resistivities of the oxidized ($\delta \ll x$, set A) samples. The samples are semiconducting for $x \leq 0{\cdot}5$, and metallic for $x = 1$. For $x = 0{\cdot}8$, the sample displays metal-like properties down to 205 K where an M–I transition occurs, which was found from susceptibility measurements to correspond to AF ordering. Only $x = 0{\cdot}8$ ($T_N = 205$ K) and $x = 1{\cdot}0$ ($T_N = 130$ K) samples display a pure AF transition. In the semiconducting samples, this AF transition is accompanied by parasitic ferromagnetism due to spin canting.

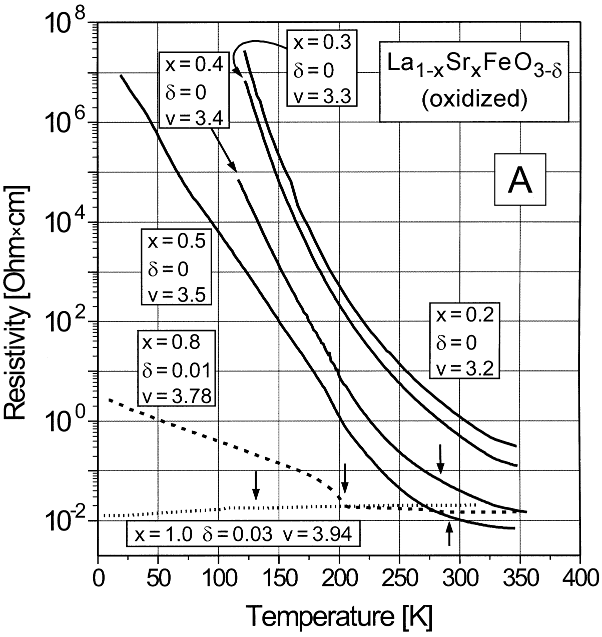

Fig. 1. Resistivity versus temperature of 'oxidized' $(La_{1-x}Sr_x)FeO_{3-\delta}$ ($\delta \ll x$). Arrows indicate magnetic transitions.

Very similar behavior of set A, as a function of v, is observed at the higher valencies when δ is used as a parameter for $x = 1{\cdot}0$ (Fig. 2, set B). For $v = 3{\cdot}64$ ($\delta = 0.18$), the sample exhibits an M–I transition accompanied by AF ordering (from susceptibility measurements) at $T_N = 75$ K. However, for $3{\cdot}2 \leq v \leq 3{\cdot}4$, no systematic trend of the resistivity with varying v can be observed. The corresponding susceptibility measurements all showed a transition to parasitic ferromagnetism at 230 K, like that observed in the $v = 3{\cdot}5$ ($\delta = 0{\cdot}25$) sample, with

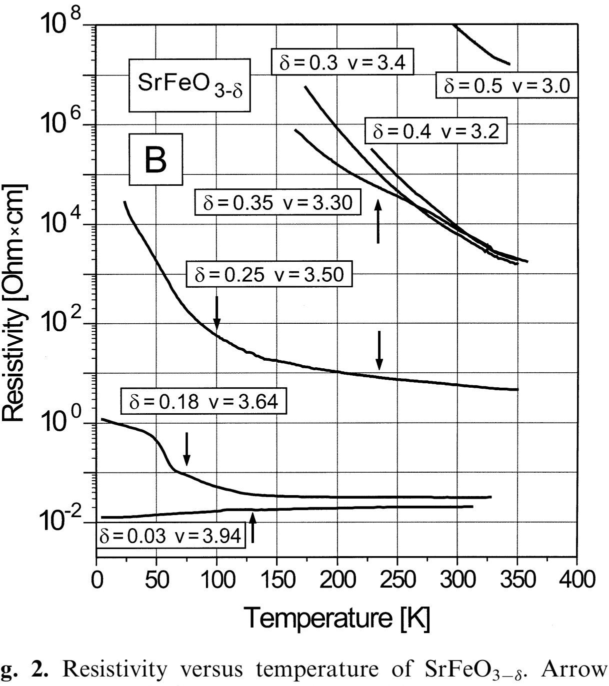

Fig. 2. Resistivity versus temperature of $SrFeO_{3-\delta}$. Arrows indicate magnetic transitions.

magnetization decreasing with increasing δ. This is indicative of a two-phase system, and also agrees with the observed powder XRD spectra, which shows reflections from both the $v = 3$ ($SrFeO_{2\cdot5}$) and $v = 3\cdot5$ ($SrFeO_{2\cdot75}$) phases in changing proportions.

The results obtained for $x = 0\cdot8$ with δ as a parameter (Fig. 3, set C) are comparable to the previous data sets when v is used as the determining parameter: for $v \geq 3\cdot64$, M–I transitions occur at $T_N = 205$ and 200 K, whereas the samples are semiconducting at lower v. For $v = 3\cdot5$, a transition to parasitic ferromagnetism is observed at 220 K, and the resistivity exhibits a temperature dependence similar to that of the other samples with the same valency (from sets A and B). For $v \leq 3\cdot2$, additional lines appear on the XRD spectra, which can be attributed to either oxygen vacancy or phase separation.

Our results indicate that the $(La,Sr)FeO_{3-\delta}$ system is controlled essentially by the valency of Fe, as compounds with similar valencies obtained with different (x, δ) combinations show the same features. At v close to 4·0 ($SrFeO_3$), the behavior is metallic down to 4 K, which agrees with data reported elsewhere,[6] with a change in the slope of the resistivity–temperature curve at T_N. Slightly lower-valency compositions occur near the $v = 3\cdot6$ to 3·8 range. ($SrFeO_{2\cdot82}$, $La_{0\cdot2}Sr_{0\cdot8}FeO_3$, and $La_{0\cdot2}Sr_{0\cdot8}FeO_{2\cdot92}$) all exhibit sharp M–I transitions at T_N. The interpretation is complicated by the occurrence of C ordering,[1,7] which influences the AF transition and possibly gives rise to parasitic ferromagnetism. In single-phase compounds, (by XRD) with $3\cdot4 \leq v \leq 3\cdot5$, the resistivity progressively changes slope near 300 K, which corresponds to an observed transition in the magnetic susceptibility.

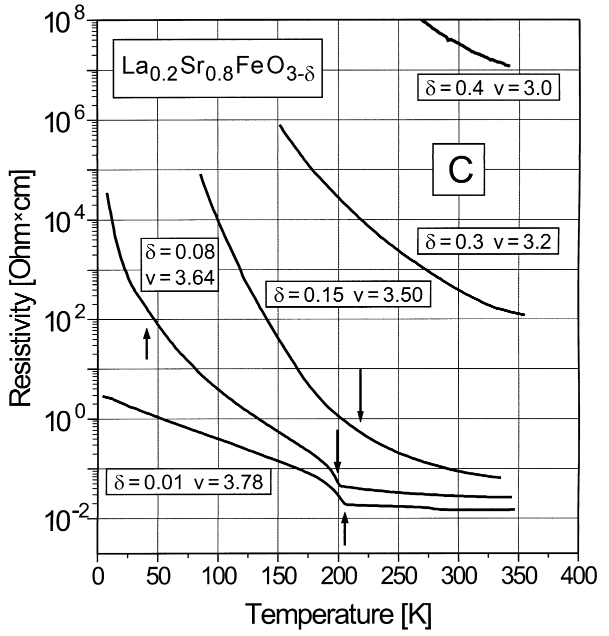

Fig. 3. Resistivity versus temperature of $(La_{0\cdot2}Sr_{0\cdot8})FeO_{3-\delta}$. Arrows indicate magnetic transitions.

One can schematize the behavior of the resistivity, phase stability, and valency in a single ternary phase diagram, as shown in Fig. 4.

3.2 Manganates

Figure 5 shows the resistivity data of the as-prepared (in air, set D) and oxygen-annealed (set E) manganate samples, with corresponding T_c of the F transitions. All samples with $x > 0$ are ferromagnetic, whereas $LaMnO_3$ exhibits parasitic F ordering at 150 K. Oxygen annealing enhances the conductivity for low x values and at low temperature, although a complementary thermogravimetric experiment on the $x = 0\cdot10$ compound did not show a measurable ($> 0\cdot01$) variation of the overall value of δ after 2 days at 500 °C in pure oxygen. The effect of reduction of $(La_{0\cdot4}Sr_{0\cdot6})MnO_{3-\delta}$ (set F) is shown in Fig. 6. The most reduced sample ($\delta = 0\cdot24$, $v = 3\cdot12$) is semiconducting as expected from its low valency. However, a clear F metallic behavior is not exhibited by the intermediate reduction levels to $\delta = 0\cdot20$ ($v = 3\cdot20$) and $\delta = 0\cdot10$ ($v = 3\cdot40$). The resistivity compared to that of the oxidized samples with the same valency is very high, with the resistive and magnetic transitions smeared out over a broad temperature range. All compounds are perovskite single phase by XRD, but reduction leads to an increase in the lattice parameters, as measured from the powder spectra, with tetragonal splitting at $\delta = 0\cdot24$ ($v = 3\cdot12$).

In contrast to the ferrates, the valency alone therefore does not determine the electrical and magnetic behavior of the $(La_{1-x}Sr_{0\cdot6})MnO_{3-\delta}$ system, as compounds obtained by reduction of $(La_{0\cdot4}Sr_{0\cdot6})MnO_{3-\delta}$ are significantly different from their same-valency oxidized counterparts. The effects of oxygen hyperstoichiometry cannot be responsible for this because for $x = 0\cdot3$, δ approaches 0.[5] Obviously, the additional disorder introduced by combining cation doping sites and oxygen vacancies has a strong effect. In addition, the observed dilation

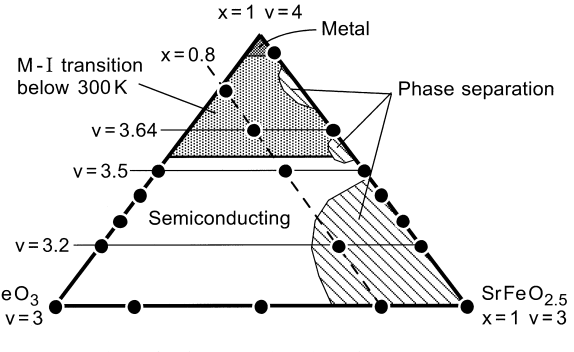

Fig. 4. Synopsis of the results in the ternary $LaFeO_3$–$SrFeO_{2\cdot5}$–$SrFeO_3$ phase diagram, with experimental points shown as dots. Phase separation for $SrFeO_{2\cdot75-2\cdot82}$ and $SrFeO_{2\cdot86-2\cdot97}$ ranges according to Ref. 2.

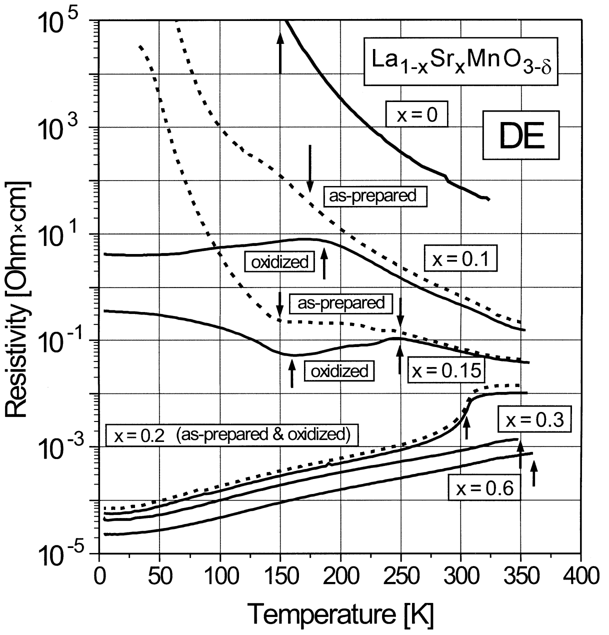

Fig. 5. Resistivity versus temperature of $(La_{1-x}Sr_x)MnO_{3-\delta}$, as-prepared (dashed) and annealed at 500 °C in O_2. Arrows indicate magnetic transitions.

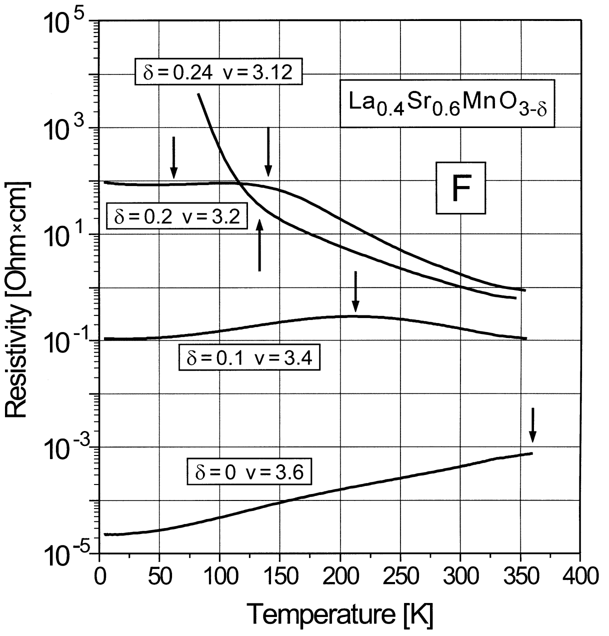

Fig. 6. Resistivity versus temperature of $(La_{.4}Sr_{0{\cdot}6})MnO_{3-\delta}$. Arrows indicate magnetic transitions.

of the lattice upon reduction may contribute. The effect of ‘oxidation’ at 500 °C O_2 for low x values cannot be ascribed to valency change alone, as absolutely no weight change was detected for $x = 0{\cdot}1$. Rearrangement of defects such as metal vacancies could play a role, as ‘oxygen hyperstoichiometry’ really corresponds to the presence of double cation vacancies in a filled oxygen sublattice.[5]

4 Conclusions

The resistivity in the $(La_{1-x}Sr_x)FeO_{3-\delta}$ system was found to be essentially controlled by the Fe valency, with properties ranging from insulating ($v = 3$) to semiconducting ($3{\cdot}2 \leq v \leq 3{\cdot}5$) to metallic with M–I transitions at low temperature ($3{\cdot}64 \leq v \leq 3{\cdot}78$) to metallic ($v = 3{\cdot}94$). The interpretation of the results for the manganate $(La_{1-x}Sr_x)MnO_{3-\delta}$ system is not as straightforward, as the electrical and magnetic behavior is not controlled by valency alone, but is significantly affected by the additional disorder introduced by the presence of oxygen vacancies.

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