2003

Zinc doping effects on the structure, transport and magnetic properties of La0.7Sr0.3Mn1-xZnxO3 manganite oxide

E V. Sotirova-Haralambeva
University of Wollongong

Xiaolin Wang
University of Wollongong, xiaolin@uow.edu.au

Hua-Kun Liu
University of Wollongong, hua@uow.edu.au

Tania M. Silver
University of Wollongong, tsilver@uow.edu.au

Konstantin Konstantinov
University of Wollongong, konstan@uow.edu.au

See next page for additional authors

Recommended Citation

Sotirova-Haralambeva, E V.; Wang, Xiaolin; Liu, Hua-Kun; Silver, Tania M.; Konstantinov, Konstantin; and Horvat, Josip, "Zinc doping effects on the structure, transport and magnetic properties of La0.7Sr0.3Mn1-xZnxO3 manganite oxide" (2003). *Australian Institute for Innovative Materials - Papers*. 1164.
https://ro.uow.edu.au/aiimpapers/1164

Zinc doping effects on the structure, transport and magnetic properties of La0.7Sr0.3Mn1-xZnxO3 manganite oxide

Abstract

The processing, microstructures and properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ perovskite manganite, with x=0, 0.1, 0.2, and 0.3 have been investigated. X-ray diffraction, scanning electron microscopy (SEM) and other characterisation methods were used to study the relations of microstructure and properties. The X-ray powder diffraction results show a single phase for the 0<<em>x<0.3 region that confirms the zinc incorporation into the Mn site. The SEM images with magnification 1500× indicate that the studied system is a single phase. The transport measurements show decreasing of insulator to metal transition temperature, T_t, with increasing the zinc concentration on the Mn site, while the resistivity increases with increasing the zinc doping level for 0<<em>x<0.1. The maximum resistivities are found at 380 and 160 K, respectively.

The PPMS measurements show that the magnetisation value is greatest for x=0.1 and drastically decrease for the parent material, as well as with increasing the zinc doping concentration above 20%, when the compound changes from ferromagnetic to paramagnetic. The paramagnetic to ferromagnetic transition temperature variations, T_c, agrees with the insulator to metal variations, T_t, from the transport measurements for the parent and 10% doped material. For zinc doping levels above 20%, the behavior of the studied system changes from ferromagnetic to paramagnetic.

Keywords

manganite, xznxo3, 3mn1, 7sr0, la0, oxide, properties, zinc, magnetic, transport, structure, effects, doping

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Sotirova-Haralambeva, E. V., Wang, X. L., Liu, K. H., Silver, T., Konstantinov, K. & Horvat, J. (2003). Zinc doping effects on the structure, transport and magnetic properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ manganite oxide. Science and Technology of Advanced Materials, 4 149-152.

Authors

E V. Sotirova-Haralambeva, Xiaolin Wang, Hua-Kun Liu, Tania M. Silver, Konstantin Konstantinov, and Josip Horvat

ELSEVIER

Science and Technology of Advanced Materials 4 (2003) 149–152

SCIENCE AND TECHNOLOGY OF ADVANCED MATERIALS
www.elsevier.com/locate/stam

Zinc doping effects on the structure, transport and magnetic properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ manganite oxide

E.V. Sotirova-Haralambeva*, X.L. Wang, K.H. Liu, T. Silver, K. Konstantinov, J. Horvat

Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia

Received 1 February 2003; accepted 13 February 2003

Abstract

The processing, microstructures and properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ perovskite manganite, with $x = 0$, 0.1, 0.2, and 0.3 have been investigated. X-ray diffraction, scanning electron microscopy (SEM) and other characterisation methods were used to study the relations of microstructure and properties. The X-ray powder diffraction results show a single phase for the $0 < x < 0.3$ region that confirms the zinc incorporation into the Mn site. The SEM images with magnification 1500 × indicate that the studied system is a single phase. The transport measurements show decreasing of insulator to metal transition temperature, T_t, with increasing the zinc concentration on the Mn site, while the resistivity increases with increasing the zinc doping level for $0 < x < 0.1$. The maximum resistivities are found at 380 and 160 K, respectively.

The PPMS measurements show that the magnetisation value is greatest for $x = 0.1$ and drastically decrease for the parent material, as well as with increasing the zinc doping concentration above 20%, when the compound changes from ferromagnetic to paramagnetic. The paramagnetic to ferromagnetic transition temperature variations, T_c, agrees with the insulator to metal variations, T_t, from the transport measurements for the parent and 10% doped material. For zinc doping levels above 20%, the behavior of the studied system changes from ferromagnetic to paramagnetic.

Keywords: Zinc doping; CMR materials; Perovskites

---

1. Introduction

The CMR materials are manganite perovskites with various chemical compositions. Such materials are very interesting for both fundamental reasons as well as for their prospects for practical applications [1–21]. $LaMnO_3$ manganite oxide [1–3] is an insulator with a perovskite crystal structure. When we dope it with divalent ions ($I = Ca^{2+}$, Sr^{2+}, Ba^{2+}, Pb^{2+}), we obtain a $La_{1-x}I_xMnO_3$ system [4,5] that shows a very large negative magnetoresistance. Because of their magnetoresistive properties, both systems—the parent $LaMnO_3$, and the doped $La_{1-x}I_xMnO_3$ oxides have been interesting for research for material engineers and physicists since 1951 [1–5]. An applied magnetic field changes dramatically the electrical resistance of these two groups of oxides [6,7]. Achieving giant magnetoresistance response at room temperature as well as in small magnetic fields are the physical properties that are the base for technological applications [6–8]. Chemical substitution [2] is one of the methods used for improving and optimising these two viable parameters. $La_{1-x}Sr_xMnO_3$ is a hole-doped oxide with perovskite structure known to be a conducting ferromagnet [5,9]. The giant magnetoresistance effect (GMR) observed in $La_{1-x}Sr_xMnO_3$ [10,11] can be interpreted by the so-called double exchange mechanism [12]. It involves a transfer of an electron from the Mn^{3+} site to the central oxide ion and simultaneously another electron's transfer from the oxide ion to the Mn^{4+} site. Study of the electronic structure of $La_{1-x}Sr_xMnO_3$ oxide [13,14] has shown that Zener's double exchange interaction plays a predominant role between Mn^{3+} and Mn^{4+} ions. It has been suggested that the resistivity of the $La_{1-x}Sr_xMnO_3$ system cannot be explained only by the double exchange mechanism, and proposed that polaron effect arising from the Jahn–Teller splitting of the Mn^{3+} ion plays the very important role [15]. The Mn site is the heart of the double exchange; however, most of the investigations have

---

* Corresponding author.
E-mail address: evs01@uow.edu.au (E.V. Sotirova-Haralambeva).

1468-6996/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S1468-6996(03)00028-7

been centered on doping of the La site. We studied the effects of Mn substitution with 10–30% zinc on the crystal structure, transport and magnetic properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ systems as a continuation of our investigation of structure, transport, paramagnetic and ferromagnetic properties of $La_{0.8}Sr_{0.2}Mn_{1-x}Zn_xO_3$ perovskite manganite [16,17].

2. Experimental procedures

The solid state reaction was used for preparation of polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ with $x = 0$, 0.1, 0.2 and 0.3. Proportions of appropriately high purity (99.9%) oxides of La_2O_3, Mn_2O_3, and ZnO, and carbonate of $SrCO_3$, were weighted according to the nominal compositions of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ with $x = 0$, 0.1, 0.2 and 0.3. Mixed thoroughly, ground, and pressed into pellets 10 mm in diameter, these powders were sintered twice at 1200 and 1250 °C for 10 h with one intermediate grinding and mixing step. A Philips PW 1730 phase XRD machine and a Leica 40 Stereo Scan microscope were used for characterisation of the crystal structure of these materials.

Their resistivity was measured as a function of temperature in a null magnetic field using the four-probe technique between 30 and 380 K. The samples were cut in a rectangular shape. The four contacts were prepared with silver paste, and put in the furnace for an hour at 300 °C. A copper-constant thermocouple placed in the vicinity of the sample controlled its temperature.

The Physical Properties Measurement System (PPMS), Quantum Design performed the magnetic measurements of zero-field cooled (ZFC) and field-cooled (FC) magnetisation between 4.2 and 350 K at a magnetic field of 50 Oe.

3. Results and discussion

The structural characterisation of the samples performed by the XRD measurements show a clean single orthorhombic phase for the $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ samples with $x = 0$, 0.1, 0.2 and 0.3 which confirms the zinc incorporation into the Mn site. In Fig. 1 we plotted the X-ray diffraction patterns of all polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ with $x = 0$, 0.1, 0.2 and 0.3. The scanning electron microscopy (SEM) measurements were performed for sample identification and characterisation of the standard undoped and doped samples with $x < 0.2$. Their morphology is shown in Fig. 2 by backscattered and secondary electron images, using a magnification of 1500 ×. The bar scale represents 2 μm. These images show that the material is a single phase one, porous with a small grain size of about 1–3 μm. Fig. 3 shows the resistivity–temperature plots of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ with $x = 0$, and 0.1 in a null magnetic field. It can be seen that the resistivity of the parent oxide gradually increases with increasing the temperature from 30 to 380 K, however, for 10% zinc concentration the behavior is different from that of the parent material. The resistivity increases to a maximum at 160 K, then sharply decreases as the temperature is increased to 380 K. Moreover, the resistivity of the doped material ($x = 0.1$) is with several orders of magnitude greater than the resistivity of the parent composition ($x = 0$). The maximum resistivities are found at 160 and 380 K, respectively. The insulator to metal transition temperature, T_t, decreases with increasing the zinc concentration, while the resistivity of this system increases with increasing the zinc content. Fig. 4 shows the temperature dependence of the magnetisation measured at a magnetic field of 50 Oe between 4.2 and 350 K for the polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ for

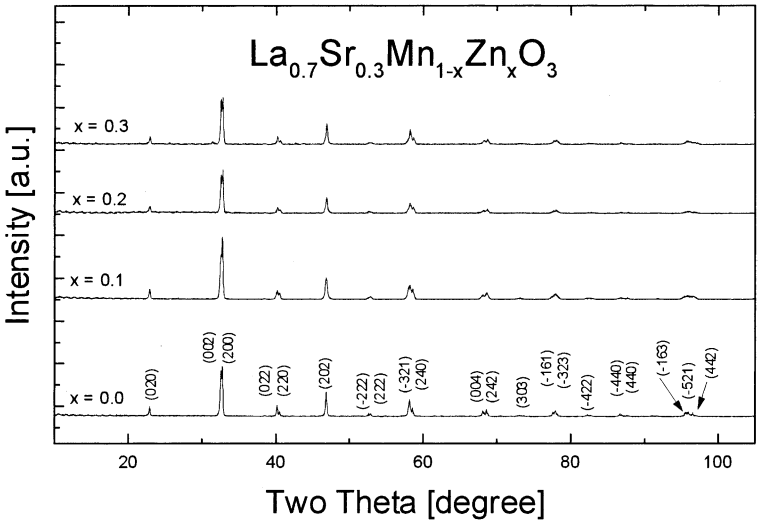

Fig. 1. X-ray powder diffraction patterns of standard and doped polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ for $x = 0$, 0.1, 0.2, and 0.3.

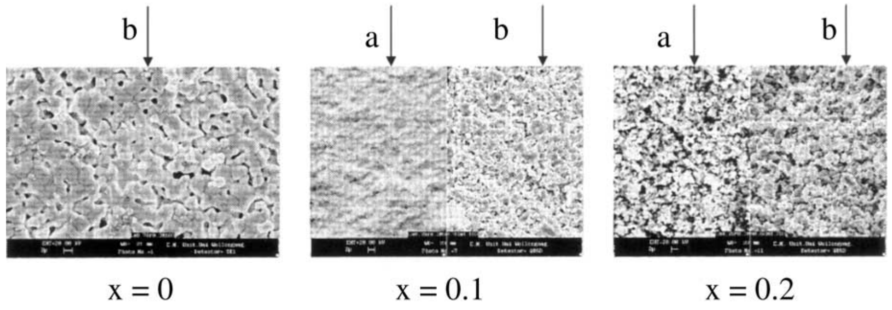

Fig. 2. Back scattered (a) and secondary (b) electron images with magnification 1500 × of polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ for $x = 0$, 0.1, and 0.2. The bar scale represents 2 μm.

$x = 0$, 0.1, 0.2, and 0.3. The magnetisation increases in the doped $La_{0.7}Sr_{0.3}Mn_{0.9}Zn_{0.1}O_3$ material when the temperature is decreased from 350 to 4.2 K with the material showing ferromagnetic behavior over this temperature range, while the parent, 20%, and 30% zinc doped materials show lower magnetisation values over the studied temperature range.

The magnetisation value is greatest for $x = 0.1$ and drastically decrease for the parent material, as well as with increasing the zinc doping concentration above 20%, when the compound changes to paramagnetic.

It is believed that double exchange plays an important role between the Mn^{3+} and Mn^{4+} in CMR materials, and $La_{0.7}Sr_{0.3}MnO_3$ in particular. Therefore, when we dope the Mn site with nonmagnetic ion, such as zinc is, the double exchange proposed by Zener in 1951 [12] is weakened dramatically, because the sites occupied by zinc ions can no loner participate in it [18–20]. There is a possibility for cluster formation in the LaSrMnZnO system, similar to LaCaMnZnO one [18], when the zinc ion substitutes the Mn site that could lead to reducing the T_c with increasing the zinc concentration.

4. Summary

The relations of microstructure and properties of zinc doped $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ system with $x = 0$, 0.1, 0.2, and 0.3 has been investigated using X-ray diffraction patterns, SEM images, transport and magnetic properties measurements. The solid state reaction was used for preparation of the studied polycrystalline samples.

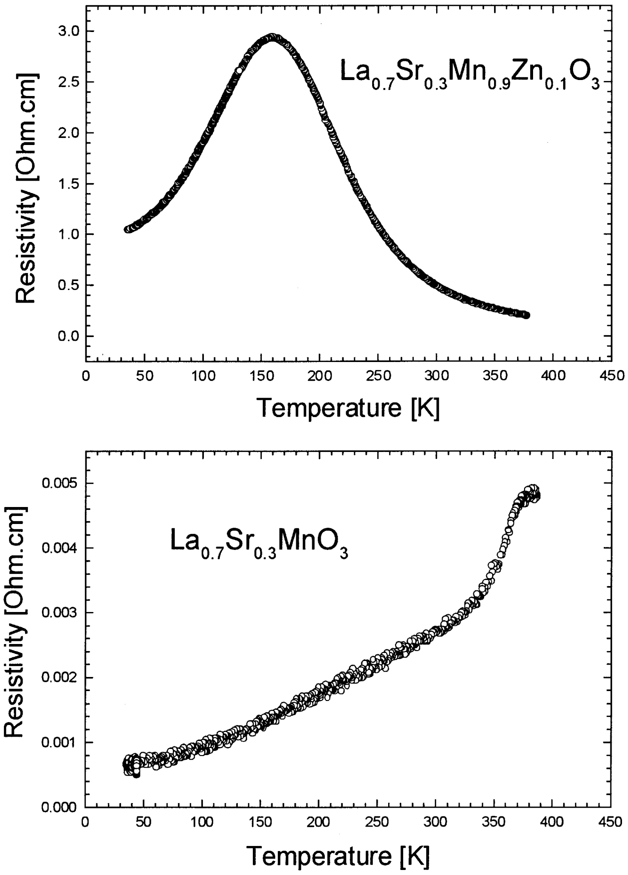

Fig. 3. Resistivity–temperature plots between 30 and 380 K of standard and zinc doped polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ for $x = 0$, and 0.1.

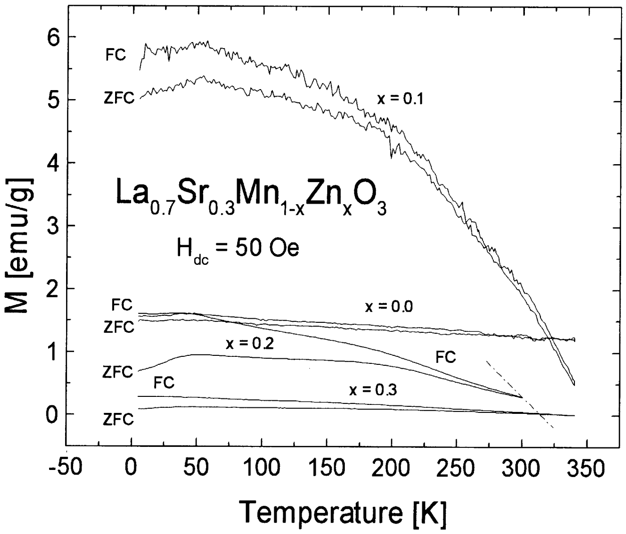

Fig. 4. Temperature dependence of the magnetisation measured in a dc field of 50 Oe between 4.2 and 350 K for the polycrystalline samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ for $x = 0$, 0.1, 0.2, and 0.3.

The patterns from the X-ray powder diffraction show a single orthorhombic phase for the $0 < x < 0.3$ region that confirms that zinc incorporates into the Mn site. Sample identification and characterisation of the standard undoped and doped samples with $x < 0.2$ was performed by using backscattered and secondary electron images. They show that the material is a single phase one, porous with a small grain size of about 1–3 μm.

From the transport measurements we can conclude that the insulator to metal temperature, T_t, as well as the resistivity is strongly composition dependent. T_t decreases with increasing the zinc doping, while the resistivity increases with increasing zinc substitution in the Mn site. The polycrystalline samples have similar granularity, so we can discuss the increase in ρ regardless of any grain boundary effects. The compound changes from ferromagnetic to paramagnetic for $x > 0.2$. The possible mechanism behind the effects of zinc doping into the $La_{0.8}Sr_{0.2}Mn_{1-x}Zn_xO_3$ system involves degradation of the double exchange between Mn^{3+}–O–Mn^{4+} in this compound. For the parent manganite oxide ($x = 0$) we have Zener's double exchange mechanism [12] between the manganese and oxygen ions: Mn^{3+}–O–Mn^{4+}. It involves a transfer of an electron from the Mn^{3+} site to the intervening oxygen ion together with another simultaneous electron transfer from the oxygen ion to the Mn^{4+} site. Introducing a very small concentration of zinc influences the double exchange because the nonmagnetic zinc ion can not participate in the double exchange: Mn^{3+}–O–Zn^{2+}. Increasing the zinc doping changes the Mn^{3+}/Mn^{4+} ratio with the amount of Mn^{4+} increasing in a linear way with increasing Zn^{2+} doping.

The magnetisation curves from the physical property measurements indicate that the paramagnetic to ferromagnetic transitions vary in temperature and depend on the zinc concentration. The paramagnetic to ferromagnetic transition temperature, T_c, defined from the PPMS measurements decreases with increasing the zinc levels. The highest value of the magnetisation is for $x = 1$.

Increasing the zinc concentration above 20% lowers the magnetisation values, and material shows only paramagnetic behavior.

CMR is a group of promising materials for signal recording and other electronic applications. Understanding and developing these materials are of both scientific and applied importance. Chemical substitution is an important way of increasing our understanding of these materials. Doping the $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ system with zinc structurally tunes and changes its properties, as we have shown. There are still many unanswered questions connected with the theory of colossal magnetoresistance. Degradation of the double exchange between Mn^{3+}–O–Mn^{4+} in $La_{0.7}Sr_{0.3}Mn_{1-x}Zn_xO_3$ system [18–20] is a possible mechanism behind the effects of zinc doping into this compound. Mn ions are replaced by nonmagnetic ions that cannot participate in the exchange [16–21] and thus act as a barrier to electron transport.

References

[1] H.Y. Hwang, S.-W. Cheong, P.G. Radaelli, M. Marezio, B. Batlogg, Physical Review Letters 75 (5) (1995) 914–917.

[2] D. Feinberg, P. Germain, M. Grilli, G. Seibold, Physical Review B 57 (10) (1998) R5583–R5586.

[3] A. Paolone, P. Roy, A. Pimenov, A. Loidl, O.K. Melnikov, A.Ya. Shapiro, Physical Review B 61 (17) (2000) 11255–11258.

[4] R. Von Helmolt, J. Wecker, B. Holzapfel, L. Scultz, K. Samwer, Physical Review Letters 71 (14) (1993) 2331–2333.

[5] E.O. Wollan, W.C. Koehler, Physical Review 100 (2) (1955) 545–563.

[6] B. Raveau, in: C.N.R. Rao, B. Raveau (Eds.), Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides, Second ed., World Scientific, Singapore, 1998, pp. 43–82.

[7] B. Raveau, A. Maignan, C. Martin, M. Hervieu, Chemistry of Materials 10 (10) (1998) 2641–2652.

[8] J.Z. Sun, Philosophical Transactions of the Royal Society of London A 356 (1998) 1693–1712.

[9] G.H. Jonker, J.H. Van Santen, Physica 16 (3) (1950) 337–349.

[10] Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamutsu, G. Kido, N. Furukawa, Journal of the Physical Society of Japan 63 (11) (1994) 3931–3935.

[11] A. Urushibara, Y. Moritomo, T. Arima, A. Asamutsu, G. Kido, Y. Tokura, Physical Review B 51 (20) (1995) 14103–14109.

[12] C. Zener, Physical Review 82 (3) (1951) 403–405.

[13] A. Chainani, M. Mathew, D.D. Sarma, Physical Review B 47 (23) (1993) 15397–15403.

[14] T. Saitoh, A.E. Boquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, Y. Takeda, M. Takano, Physical Review B 51 (20) (1995) 13942–13951.

[15] A.J. Millis, P.B. Littlewood, B.I. Shraiman, Physical Review Letters 74 (25) (1995) 5144–5147.

[16] E.V. Sotirova-Haralambeva, Synthesis, structures, transport and magnetic properties in zinc doped $La_{0.8}Sr0_{0.2}MnO_3$ perovskite manganite, Master Thesis, University of Wollongong, Australia, 2001

[17] E. Sotirova, X.L. Wang, J. Horvat, T. Silver, K. Konstantinov, H.K. Liu, Supercond. Sci. and Technol. 15 (2002) 346–350.

[18] M.X. Xu, Z.K. Jiao, Journal of Materials Science Letters 18 (18) (1999) 1307–1309.

[19] C. Zhu, R. Zheng, Journal of Physics: Condensed Matter 11 (1999) 8505–8510.

[20] V.P.S. Awana, E. Schmitt, E. Gmelin, A. Gupta, A. Sedky, A.V. Narlikar, O.F. de Lima, C.A. Cardiso, S.K. Malik, W.B. Yelon, Journal of Applied Physics 87 (9) (2000) 5034–5036.

[21] J.B. Goodenough, Physial Review 100 (2) (1955) 564–573.