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Zr-substitution effects on physical properties of the colossal magnetoresistance compounds $La_{2/3}Sr_{1/3}MnO_3$

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We present a detailed study of the polycrystalline perovskite manganites $La_{2/3}Sr_{1/3}Zr_xMn_{1-x}O_3$ (x = 0, 0.1, 0.15, 0.2, 0.25, 0.3) at low temperatures and high magnetic fields, including electrical resistance, and magnetization. The static magnetic susceptibility was also measured up to 900 K. All the samples show large negative magnetoresistance behavior. The Curie temperatures decrease with Zr doping. Our results show the decrease of Mn^{4+}/Mn^{3+} ratio, and this lead to the decrease of the number of ferromagnetic Mn^{4+}- O - Mn^{3+} interaction. The data suggest that the magnetoresistance of the system is dominated by intergranular effects, but some intrinsic effects have also to be considered, as the temperature approach T_c. This appears to be a consequence of the structural and magnetic disorder created by the random distribution of Zr atoms.

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1. Introduction

The perovskite manganese oxides like $La_{1-x}Sr_xMnO_3$ (LSMO), display a number of remarkable anomalously magnetic and transport properties including a large negative magnetoresistance, the so-called "colossal" magnetoresistance (CMR) effect [1,2]. The richness of the phase diagrams of these materials was considered to be determined by the competition of double exchange and superexchange interactions, charge/orbital ordering instabilities, and strong coupling to the lattice deformations. This coupling has recently been shown to commonly result in electronic phase separation between different magnetoelectronic states at low temperatures [3,4]. The electronic properties of LSMO, are nearly half metallic [1,5]. The compound with x = 0.3 was found to have a high transition temperature (T_c ~370 K) into ferromagnetic state that makes this compound of great importance for applications in spintronics. This compound shows a metal-like behaviour of resistivity bellow T_c, and a maximum of magnetoresistance around T_c [1,2].

Since the behavior of the Mn ions are responsible for the electrical and magnetic properties of this compound, it is interesting to change the distance between Mn ions in the compound as well as the Mn^{3+}/ Mn^{4+} ratio and to introduce disorder in the Mn lattice. Substitution of manganese with four-valent ion such as Zr^{4+} leads to the decrease of Mn^{4+}/Mn^{3+} ratio and reduces the role of the interaction between Mn^{4+}- Mn^{3+} ions.

In this paper we analyze the structural, electrical and magnetic properties of the $La_{2/3}Sr_{1/.3}Zr_xMn_{1-x}O_3$) series.

2. Experimental

Polycrystalline samples with nominal composition $La_{2/3}Sr_{1/.3}Zr_xMn_{1-x}O_3$ (x = 0, 0.1, 0.15, 0.2, 0.25, 0.3) were prepared by standard ceramic reaction. The compounds were sintered in air at 1400 ^oC for 24 h.

The phase and lattice parameters of the compounds were determined by X-ray powder diffraction using CuK radiation with a Brucker Advance D8 AXS diffractometer.

The resistivity was measured in a cryogen-free magnet cryostat CFM-7 (Cryogenic Ltd.) in magnetic fields up to 6 T and in the temperature range from 5 K to 300 K. We used a Weiss-Forrer equipment to measure the dc susceptibility in the range from 300 to 950 K. This latter equipment was also used to find the Curie temperatures of the samples.

3. Results and discussions

The X-ray diffraction patterns of $La_{2/3}Sr_{1/.3}Zr_xMn_{1-x}O_3$ showed that the compounds are mainly clean single phase, within the limit of experimental errors. The lattice parameters are indicated in Table 1 together with some other data. All the compounds are in a rhombohedral structure, and here the system is described with a hexagonal cell. The lattice parameters are nearly unchanged upon doping, due to relatively closed values of the ionic radii for Mn^{+4} and Zr^{4+}.

Table 1. Quantitative data for the $La_{2/3}Sr_{1/.3}Zr_xMn_{1-x}O_3$ system.

Sample x	a (Å)	b (Å)	c (Å)	V (Å^3)	MR* (%)	T_{max} (K)	T_c (K)	$f_{Mn^{4+}}$ (%)
0.00	5.496	5.496	13.372	349.8	66.11	250	355	36.65
0.10	5.511	5.511	13.370	351.9	60.50	254	353	30.76
0.15	5.508	5.508	13.377	351.6	59.33	272	349	27.20
0.20	5.490	5.490	13.338	348.0	56.92	273	340	23.18
0.25	5.514	5.514	13.380	352.3	54.72	240	336	18.39
0.30	5.513	5.513	13.381	352.3	51.37	270	333	11.54

*) MR = (R(0 T)-R(6 T))/R(0 T) taken at 75 K.

For all the samples the resistivity decreases in high magnetic field. In Fig. 1 we show the variation of the resistivity, $\rho(H)/\rho(0)$, with the applied magnetic fields at 75 K for the studied compounds.

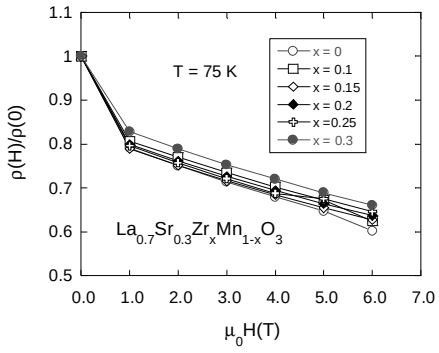

Fig. 1. $\rho(H)/\rho(0)$ curves for $La_{2/3}Sr_{1/3}Zr_xMn_{1-x}O_3$ system at 75 K.

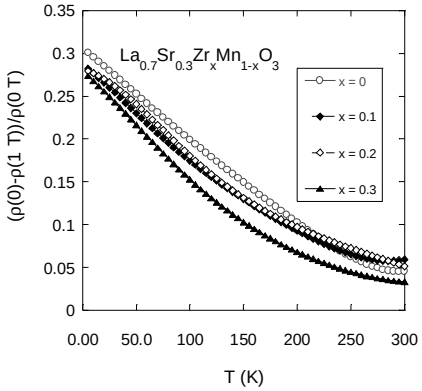

Fig. 3. The magnetoresitance as a function of temperature for some of the studied samples.

The resistivity increases with increasing temperature, then it shows a maximum at T_{max} in the range 240-275 K. This behavior is shown in Fig. 2 for the samples with $x = 0$ and $x = 0.2$, (for the sake of clarity) in the absence of a magnetic field, and in 1 T applied field. In the low temperature region (T < 30 K) a shallow minimum appeared, that seems to be indicative of the intergrain conductivity and of the associated intergrain magnetoresitivity [6]. The temperature dependence of magnetoresistance $MR\ (T, H = 1\ T) = [\rho(T, 0\ T)-\rho(T,1\ T)]/\rho(T, 0\ T)$, for some of the samples, is plotted in Fig. 3. This dependence is not typical for a CMR effect since the magnetoresistance does not show a maximum near T_{max} and it seems to be an intergranular electrical conductivity effect [7]. These curves show that magnetoresistance rapidly increases in relatively low magnetic fields and then, in higher fields the changes are almost linear. The rapid increase of magnetoresistance in the low fields region is typical for polycrystaline manganite samples and it was explained by tunneling between AFM coupled grains [6]. The linear behavior of *MR(H)*, in the region of high fields is a result of the suppression of spin fluctuations by the applied magnetic field [6]. This linearity could be of interest for practical application, such as magnetoresistive transducers.

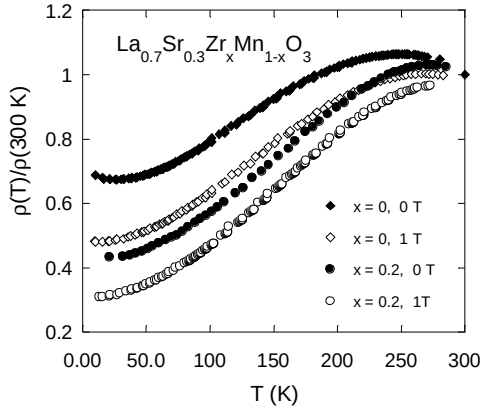

Fig. 2. $\rho(T)/\rho(0)$ curves for $La_{2/3}Sr_{1/3}Zr_xMn_{1-x}O_3$ system taken in 1 T (open symbols) and in zero applied magnetic field (solid symbols)

The T_c' s were estimated from the *M(T)* curves in low magnetic field (lower than 0.05 T) and they are displayed in Table 1. As can be seen the T_c's decrease with increasing Zr content.

The Mn^{4+} concentration, $f_{Mn}{}^{4+}$, was estimated from dc susceptibility measurements in the region of high temperature: 450 – 950 K, to avoid the occurrence of ferromagnetic clusters near by T_c. As shown in Fig. 4, at high temperatures $\chi_{dc}(T)$ follows, in all cases, a FM Curie–Weiss temperature dependence, $\chi_{dc}(T) = C/(T-\Theta)$. From the linear behavior of $\chi_{dc}{}^{-1}(T)$ we determined the Curie constants, to estimate the Mn^{4+} fraction. The values of $f_{Mn}{}^{4+}$ for each sample are also indicated in Table 1 and they decrease with increasing Zr content, from 36.65% for $x = 0$, to 11.54 % when $x = 0.3$, suggesting that Zr replaces mainly the Mn^{4+} ions.

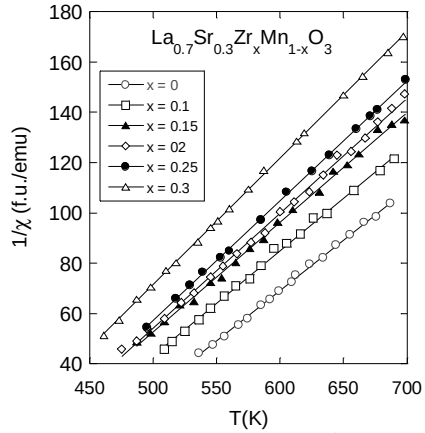

Fig. 4. Temperature dependence of the inverse susceptibilities for the $La_{2/3}Sr_{1/3}Zr_xMn_{1-x}O_3$ system. The solid lines represents the Curie-Weiss fitting to the data.

The substitution of Zr for Mn in $La_{2/3}Sr_{1/3}MnO_3$ leads to lower Curie temperatures. The decrease of T_c's with increasing doping content correlates with the decrease of Mn^{3+}/Mn^{4+} ratio, that means a reduced number of ferromagnetic Mn^{4+}-O- Mn^{3+} interactions. Also, the increase of the lengths between the Mn ions contributes to the lowering of the T_c's.

In spite of the granular nature of the samples, the changes in magnetic properties, such as temperature dependence of magnetization or magnetic susceptibility as well as the Curie temperatures, are very small in comparison with those of single crystals [6]. The difference is more significant when the electrical conductivity is concerned. For a polycrystalline sample the maximum in $\rho(T)$ occurs, as can be seen in Table 1, well bellow T_c while for a single crystal these two temperatures are very close each others. The behavior of magnetoresistance in our samples seems to be dominated by transport across the grain boundaries since it increases monotonically with decreasing temperature in the low temperature region. The upturn trend of *MR(T)* curves near by 300 K, however, suggests that magnetoresistance has also an intrinsic component as temperature approaches T_c.

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