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Structure and transport properties of $(La_{1-x-y}Y_y)_{2/3}Ca_{1/3}MnO_3$ with La-site vacancies

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Abstract: Several samples of manganese oxides $La_{(1-x)2/3}Ca_{1/3}MnO_3$ (V-LCMO) and $(La_{0.7-x}Y_{0.3})_{2/3}Ca_{1/3}MnO_3$ ($x<0.15$) (V-LYCMO) with vacancies at La-site (La-vacancy) were prepared by solid-state reaction method. The X-ray diffraction(XRD) patterns refined by Rietveld confirm that these compounds exhibit single phase structure with orthorhombic symmetry (Pnma). The lattice parameters, Mn—O bond length and Mn—O—Mn bond angle vary with La-vacancy concentration, as an indication of the occurrence of the local Jahn-Teller effect. The measurement result of V-LCMO compounds shows that the maximum magnetoresistance(MR) is about 220% at T_{IM}=268 K and La-vacancy content x=0.04. For V-LYCMO compounds, there exists metal-insulator transition at about 50 K, and a very large MR (over 10^6%) is observed at the temperature ranging from 40 K to 50 K.

Key words: $La_{(1-x)2/3}Ca_{1/3}MnO_3$; $(La_{0.7-x}Y_{0.3})_{2/3}Ca_{1/3}MnO_3$; La-vacancy; orthorhombic symmetry; Jahn-Teller effect

1 Introduction

After the giant magnetoresistance effect(GMR) was firstly observed by HELMOLT et al[1] in 1993, many research groups have tried to understand its mechanism and find new materials with better properties. Recently much attention has been paid to the perovskite manganese oxides $La_{1-x}Ca_xMnO_3$ and $Ln_{1-x}A_xMnO_3$ (Ln=La, Pr, Nd etc and A=Ca, Ba, Pb, Sr etc) with doped-vacancies[2−3]. For $La_{1-x}Ca_xMnO_3$(LCMO) compounds, ion-doped concentration will bring about different effect. Firstly, it is deemed, generally, that the Curie temperature T_C is higher at doped content x=1/3 than that at other doped contents. In addition, below T_C there exists a better ferromagnetic state and GMR effect. For $Ln_{1-x}A_xMnO_3$ compounds, T_C is very sensitive to chemical pressure of rare earth cation[4−6]. It is discussed that e_g electron hopping between Mn^{3+} and Mn^{4+} ions relates to the lattice parameters and gives rise to Jahn-Teller effect. Although doped trivalent cation doesn't change the proportion between Mn^{3+} and Mn^{4+} ions, it changes the lattice parameters and leads to the occurrence of Jahn-Teller effect. Lately there were also some studies on the influence of vacancies at A-site on structural and electromagnetic properties in perovskite manganese oxide[7−10]. Now it is necessary to analyze the influence of La-vacancies and Y-doped concentration on structures and transport properties of $La_{2/3}Ca_{1/3}MnO_3$ compounds.

2 Experimental

2.1 Samples preparation

The samples $La_{(1-x)2/3}Ca_{1/3}MnO_3$ and $(La_{0.7-x}Y_{0.3})_{2/3}$-$Ca_{1/3}MnO_3$ (x=0, 0.02, 0.04, 0.08, 0.10) compounds were prepared by solid-state reaction method. The stoichiometric mixtures of La_2O_3, Y_2O_3, $CaCO_3$ and MnO_2 powders with over 99.9% purity were ground for about 40 min, and pre-sintered at 1 000 ℃ for 12 h. The powders were ground again, and sintered at 1 350 ℃ for 24 h after pressed into pellets with a diameter of 10

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mm under 20 MPa pressure. Finally, the pellets were cooled to room temperature slowly in the furnace.

2.2 Structure measurement and refinement

The crystal structures of the samples were studied by XRD (Brucker D8, Cu K_{α}) at room temperature (300 K) and lower temperatures. The XRD spectrometer was operated at 40 kV and 20 mA, and the scanning step 2θ ranges from 20˚ to 90˚. The XRD patterns were refined by Rietveld refinement method, and the method of Rietveld refinement is similar to that of testifying super-conduct structure of rare earth materials before[11−12].

2.3 Magnetoresistance measurement

The transport properties of samples were measured by Normal Four Contacts method. The dependence of electric resistivity on the temperature was measured at zero and 8 T magnetic field, respectively. The MR is defined as:

$$MR=(\rho_0-\rho_H)/\rho_H\times 100\% \quad (1)$$

where ρ_0, ρ_H are resistance values at zero and external magnetic field, respectively[12].

3 Result and discussion

3.1 Structure parameters

The XRD patterns show that polycrystalline compounds V-LCMO and V-LYCMO (x=0, 0.02, 0.04, 0.08, 0.10) all exhibit perovskite type structure with single phase. In Fig.1, there exhibit experimental spectrum, refinement spectrum and different spectrum with their Bragg diffraction peaks. The structure parameters of the samples V-LCMO and V-LYCMO are refined by Rietveld refinement, and the refinement results of bond length and the bond angle are shown in Fig.2. It is displayed that the structures of the samples with different La-vacancy contents keep orthorhombic ($a\neq b\neq c$, $\alpha=\beta=\gamma$), space group Pnma. The lattice parameters, the Mn—O bond length and Mn—O—Mn bond angle decrease much drastically in V-LYCMO compounds than that of V-LCMO compounds. This is responsible for different mean ion radius of the La-sites with partial substitution of Y^{3+} for La^{3+}. The Y^{3+} radius (about 0.107 nm) is smaller than that of La^{3+} (about 0.122 nm) and the mean radius of La^{3+} and Ca^{3+} ions decrease with doping Y^{3+}, hence the atomic radius between A—O layer and Mn—O layer is mismatched and changes the value of tolerance factor t:

$$t=(r_A+r_O)/(r_n+r_O) \quad (2)$$

When $t<1$, the force of pressing Mn—O bond and stretching A—O bond results in Mn—O—Mn bond torsion from 180˚ to 180˚$-\varphi$. The Mn—O—Mn bond

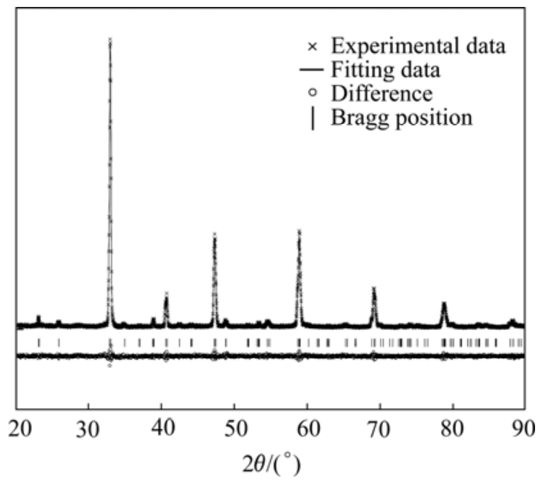

Fig.1 Typical XRD pattern, together with refined curve, different curve, and calculated Bragg positions of V-LCMO and V-LYCMO compounds

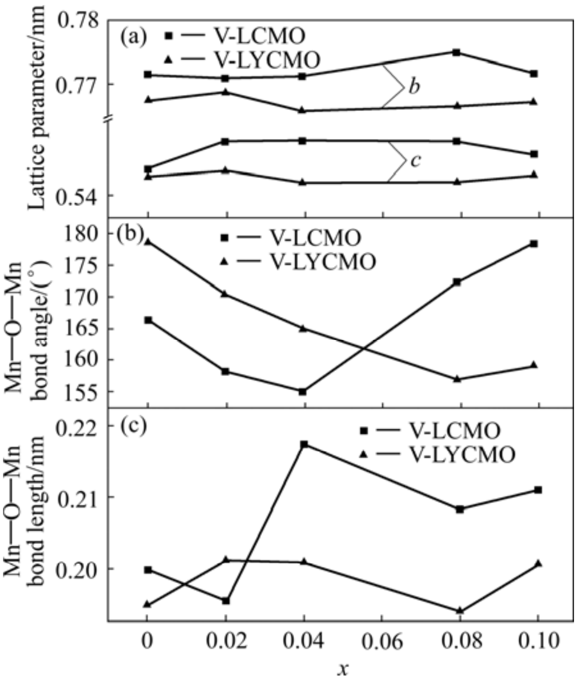

Fig.2 Dependence of lattice parameters (a), Mn—O—Mn bond angle (b) and Mn—O bond length (c) on vacancy ratio x

torsion gives rise to Jahn-Teller distortion in MnO_6 octahedron[13], and the violent coupling interaction between electron and phonon makes e_g electrons of Mn^{3+} localization due to Jahn-Teller distortion. For V-LYCMO system, it is discussed in Fig.2 that the doped vacancies change the structure parameters and affect transport properties.

3.2 Dependence of MR of V-LCMO compounds on temperature and magnetic field

For V-LCMO system, the dependence of electric resistivity on temperature at zero and 8 T magnetic field is shown in Fig.3. As shown in Fig.3(a), for the V-LCMO compounds, insulator-metal transition occurs at about 267 K, and a little of La-vacancy keeps insulator-metal transition temperature T_{IM} unchanged. Additionally, at magnetic field 8 T T_{IM} moves towards higher temperature (>300 K) and the MR is quite sensitive to external magnetic field near T_{IM}, because external magnetic field induces magnetic moments ordering to increase T_{IM} [13−15]. In Fig.3(b), for the samples of V-LCMO compounds the largest MR about 220% is observed at La-vacancy content x=0.04 and insulator-metal transition temperature T_{IM}= 268.6 K, which is almost equal to MR about 218% at 267 K without La-vacancies. Additionally, the MR value decreases dramatically and the electric resistance increases when vacancy content $x>0.04$, because La-vacancies may enhance magnetic scattering and lead to the electric resistance increasing.

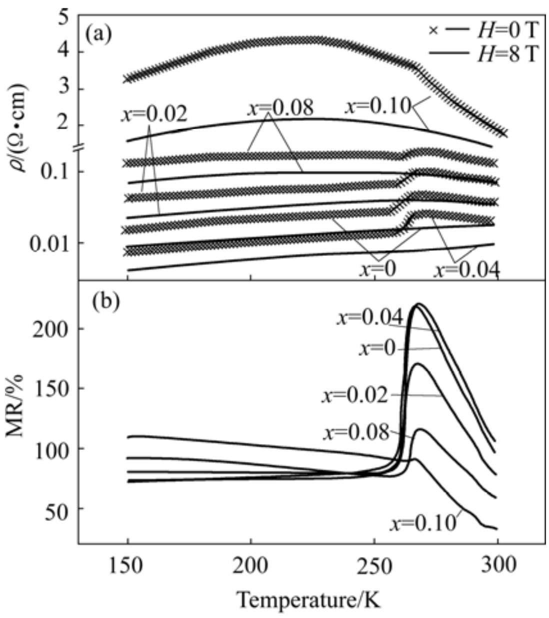

Fig.3 Dependence of electric resistivity (a) and MR (b) on temperature for V-LCMO compounds

3.3 Dependence of MR of V-YLCMO compounds on temperature and magnetic field

For the samples V-LYCMO, in Fig.4 there exhibits the dependence of electric resistivity on temperature at zero and magnetic field 8 T, respectively. As shown in Fig.4(a), the electric resistivities of the V-LYCMO compounds are up to several decuples larger than those of V-LCMO compounds. The MR value is over 10^6 in Fig.4(b), but the insulator-metal transition temperature decreases to about 50 K dramatically.

3.4 Physical mechanism of MR effect

It is well known that electric conductance of perovskite-type compounds can be understood by the

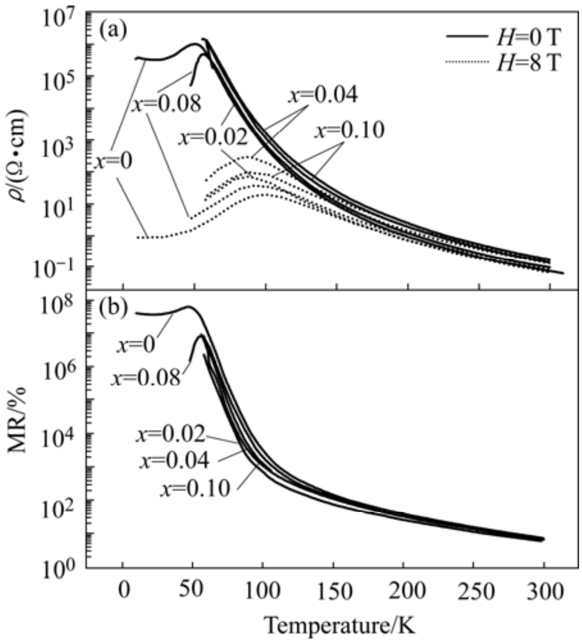

Fig.4 Dependence of electric resistivity (a) and MR (b) on temperature for V-LYCMO compounds

double-exchange mechanism under low temperature, but the double-exchange mechanism can not interpret MR behavior effectively. Millis[16] and many research groups agree that the Jahn-Teller effect with electroacoustic coupling interaction is responsible for the MR behavior.

Firstly, the Jahn-Teller effect makes e_g electrons of Mn^{3+} ion localize and results in electric resistance increasing dramatically at T_{IM}. In addition, intense electroacoustic coupling interaction changes metal into insulator above T_{IM}.

The results show that the MR effect is related to not only external magnetic field but also the doped contents. One reason may be that magnetic moments are arrayed more orderly in the high magnetic field than in the low one. The other may be that the substitution of Ca^{2+} ions for La^{3+} ions, and the proportion of Mn^{3+}/Mn^{4+} arosed by La-vacancies promote the competition between double-exchange and super-exchange interaction of Mn^{3+} and Mn^{4+}.

Additionally, the MR of V-LYCMO compounds is up to several decuples larger than that of V-LCMO compounds. On one hand, this may be that $t<1$ leads to Jahn-Teller distortion in the MnO_6 octahedron. On the other hand, ferromagnetic interaction is suppressed and antiferromagnetic interaction is enhanced with the increase of partial substitution Y^{3+} for La^{3+}, therefore, T_c moves towards lower temperature. The competition between ferromagnetism and antiferromagnetism results in spin-glass states developing, and it destroys double-exchange interaction to increase the MR values.

4 Conclusions

1) For the manganese oxides LCMO, partial substitution of Y^{3+} for La^{3+} leads to the lattice parameters, and the Mn—O bond length as well as Mn—O—Mn bond angle decreasing apparently due to the Jahn-Teller effect of MnO_6 octahedrons.

2) For the V-LCMO compounds, the electric resistance increases dramatically and the MR decreases when La-vacancy content $x>0.04$, because the vacancy concentration changes the Mn^{3+}/Mn^{4+} proportion and accelerates magnetic scattering.

3) For the V-LYCMO compounds, partial substitution of Y^{3+} for La^{3+} results in electric resistivity and the MR increasing and T_c decreasing due to the Jahn-Teller effect.

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