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Effect of Ni doping in rare-earth manganite $La_{0.7}Pb_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0.0-0.5$)

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Abstract

With Ni doping, $La_{0.7}Pb_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0-0.5$) system exhibits decrease of conductivity and increase of metal–insulator transition temperature. This is considered to occur because of the decrease of effective double exchange (DE) interaction due to Ni doping. The presence of majority of Ni^{2+} states as indicated by the XPS study, govern the transport and magnetic properties of this system. The spin-wave stiffness constant D, characterising the magnon in the low-temperature ($T < T_p$) ferromagnetic phase, estimated from the magnetisation (M) data, decreases with increasing Ni content. Unlike spin-glass-like pure insulating state below the Curie Temperature (T_C), observed in other similar transition metal ion-doped systems, magnetisation (both zero field cooled (ZFC) and field cooled (FC) measured down to 10 K) and resistivity data of the samples indicate the existence of ferromagnetic cluster-like-state, which becomes more vivid with increasing Ni doping. Like many other colossal magnetoresistive (CMR) systems, small polaron hopping conduction is observed in the high-temperature ($T > T_p$) semiconducting phase showing increase of activation energy as conductivity decreases.

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Keywords: Ni doping; Ferromagnetic-cluster; Colossal magnetoresistance; Spin-wave stiffness constant; Electron-magnon scattering

1. Introduction

Doping of transition metal ions (viz. Fe, Cr, Ni, etc.) at the Mn site [1–6] of colossal magnetoresistive (CMR) manganites is an interesting topic of study. Small change in the Mn^{3+}–O–Mn^{4+}

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network caused by transition metal ion substitution results in large changes in the magnetic and transport properties of such systems. Among the transition metal ion family, Nickel is one of the most fascinating members [7–9]. It has been observed that Ni doping at Mn site weakens ferromagnetism in the manganite system [10,11]. Substitution of Mn by Ni destroys the long-range ferromagnetic order and induces a spin-glass-like pure insulating state in the La–Sr–Mn–O system [12]. In case of Mn substitution by Ni, the combination of Ni^{2+} and Mn^{4+} has been observed to be favourable [13–15]. In the present investigation, Mn has been substituted by Ni in $La_{0.7}Pb_{0.3}MnO_3$ to study the change in the low-temperature ferromagnetic behaviour. The XPS study has been used to determine the ionic state of Ni in these compounds.

Earlier investigation of the La–Pb–Mn–O system by neutron scattering measurement shows the presence of well-defined spin waves or magnon throughout the Brillouin zone [16] at low temperature. Calculation of spin-wave stiffness constant (D) from the temperature-dependent magnetisation data also gives important information regarding the strength of microscopic magnetic coupling of the spins associated with the ferromagnetic clusters in the low-temperature [17] region. It is well known that below the Curie temperature T_C, $La_{0.7}Pb_{0.3}MnO_3$ behaves like a double-exchange (DE)-type ferromagnet. So a detailed analysis of low-temperature magnetisation data would help to throw more light on the behaviour of magnetic coupling of the spins and the importance of magnons in these DE-type ferromagnets. The Ni-doped manganite system is of particular interest for investigating the change in the spin-wave stiffness constant (D) due to weakening behaviour of the effective ferromagnetic DE interaction [11,12].

In the present work, the Ni-doped $La_{0.7}Pb_{0.3}Mn_{1-x}Ni_xO_3$-type CMR system has been carefully prepared and well characterised by structural and XPS studies. Low-temperature magnetisation and transport properties (viz. TEP and resistivity) have been measured showing the importance of electron-magnon scattering and the presence of ferromagnetic cluster-like state in the low-temperature metallic phase. High-temperature ($T > T_p$) resistivity data have been analysed to illustrate the nature of conduction mechanism in this Ni-doped system.

2. Experimental

For the preparation of bulk $La_{0.7}Pb_{0.3}Mn_{1-x}Ni_xO_3$ ($0.0 < x < 0.5$), the standard solid state reaction technique similar to our earlier work [6] has been followed. Stoichiometric amounts of La_2O_3, PbO, $Mn(C_2H_3O_2)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ (each of purity 99.99%) were taken as the starting materials. The mixtures of these raw materials were preheated in air at 773 K for 5 h. After grinding they were sintered at 1173 K for 40 h with intermediate grinding (four times). The powders of different samples thus obtained were well ground again and then pelletised and finally annealed at 1173 K for 24 h. Finally, the samples were furnace cooled to room temperature. All the samples were characterised by X-ray diffraction (XRD) with CuK_α (wavelength $\lambda = 1.541$ Å) radiation. Rietveld analysis of the diffraction data was performed using the DBWS program. Magnetisation was measured using a SQUID magnetometer down to 4 K in different magnetic fields both in field cooled (FC) and zero field cooled (ZFC) conditions. Temperature-dependent resistivity measurements (ρ) and thermoelectric power measurement were carried out using standard techniques [6] in the range of 80–425 K in 0 and 1.5 T magnetic field. All the experimental data were collected in the heating direction. Room temperature XPS (AXIS-His, KRATOS ANALYTICAL Ltd. UK) spectra were studied to confirm the ionic state of Ni.

3. Results and discussion

Room temperature XRD data of the $La_{0.7}Pb_{0.3}Mn_{1-x}Ni_xO_3$ ($x = 0.0-0.5$) system indicate rhombohedral space group ($R\bar{3}c$) with hexagonal setting ($Z = 6$). The substitution of Mn by Ni ion produces only a minor distortion in the MnO_6 octahedra. The changes in the Mn–O–Mn angles are also small (164–166° for $x = 0.0-0.5$).