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Structural and Electrical Properties of Layered Pervoskite Manganites $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.25, 0.3, 0.4$)

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Abstract: Tetragonally layered perovskite manganites of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.25, 0.3, 0.4$) were fabricated by using solid-state reaction technique. Structural characterization of the compounds was investigated by X-ray diffraction (XRD) and FT-IR absorption spectra. The XRD patterns revealed that all the samples were single phase. X-ray photoemission spectroscopy (XPS) was used to investigate their electronic structures. It was found that manganese was in mixed states of Mn^{3+} and Mn^{4+} whereas lattice oxygen and chemical absorbed oxygen were existed in all the samples. The high temperature electrical properties of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.3, 0.4$) were measured by standard four-probe technique. The results showed that both compounds had semi-conductivity behavior in the temperature range of 300 ~ 1073 K, and the electrical conduction was dominated by thermally activated behavior above 500 K.

Key words: layered perovskite manganites; crystal structure; FT-IR; resistivity; rare earths
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Layered perovskite manganites with general formula $Ln_{2-2x}R_{1+2x}Mn_2O_7$(Ln = rare earth; R = K, Ca, Sr, Ba) attract considerable attention because of their unique properties, such as colossal magneto-resistance (CMR) observed at Curie temperature (T_c), Jahn-Teller effect and metal-insulator (M-I) transition etc[1~5]. These materials are related to the $n=2$ member of the series of Ruddlesden-Popper (RP) phases[6] such as $AO(ABO_3)_n$, where n can be thought as the number of layers of vertex-sharing MnO_6 octahedra which form structural blocks along c-axis of the unit cell. It consists of two perovskite blocks of MnO_6 octahedra, separated by a rock-salt (Ln, R)O layer. The anisotropic two dimensional Mn-O-Mn networks gives rise to remarkable changes of electrical properties (largely) related to the amount of Mn^{4+}.

Recent studies on $Ln_{2-2x}R_{1+2x}Mn_2O_7$ show that the properties of the layered perovskites are very sensitive to the atom variety and concentration of the Ln and R site's ions. $La_{2-2x}Sr_{1+2x}Mn_2O_7$ and $La_{2-2x}Ca_{1+2x}Mn_2O_7$ compounds are widely studied because of their simple synthesis process and CMR effect[7~10]. However, there are few reports about the high temperature electrical property of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ in which extensive chemical control can be exercised on the magnetotransport and in which CMR is not associated with complete ferromagnetic order or zero-field metal-insulator transition[11]. In this article, tetragonally layered perovskite manganites $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x=0.25, 0.3, 0.4$) were prepared using

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solid-state reaction technique. The crystal structures, electronic structures, and high temperature electrical performances of these compounds were systematically studied.

1 Experimental

Polycrystalline $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.25, 0.3, 0.4$) were prepared by standard solid-state method. Appropriate amounts of Nd_2O_3, $SrCO_3$, and Mn_2O_3 powers were mixed thoroughly with an agate mortar and pressed into pellets. The pellets were heated at 1373 K for 24 h, 1573 K for 24 h, and 1723 K for 30 h, respectively, in air with intermediate grindings.

X-ray diffraction (XRD) patterns of the powders were obtained on Rigaku D/max-2000 diffractometer with Cu radiation ($\lambda = 0.15406$ nm) to examine the sample purities. The contents of Nd, Sr, and Mn elements were detected by XRF (Axiso pw 4400). The infrared spectrum of the polycrystalline powders of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ was recorded by PerkinElmer Spectrum One Spectrometer and a KBr-disc technique. XPS experiment was carried out on VG ESCALAB MK Ⅱ spectrometer using Al radiation ($h\nu = 1486.6$ eV) and the proportion of oxidation is simulated using program SDP v4.2 (XPS International, LLC). The electrical resistivity was measured from 300 to 1073 K using standard four-probe technique.

2 Results and Discussion

Similar to other layered manganese oxides, $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ belongs to Runddlesden-Popper compound with the $n = 2$ member of the series (Fig. 1). The XRD patterns of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.25$, 0.3, 0.4) samples are shown in Fig. 2. All the diffraction peaks can be indexed as the tetragonal structures (*I4/mmm*), and the peaks are well matched with the expected values for Ruddlesden-Popper phase (Sr, Ln)$_3Mn_2O_7$ [12]. The cell parameters were refined from the XRD data by least-square method, which are listed in Table 1. As expected, substitution of Sr^{2+} ion for Nd^{3+} ion results in the decrease of *c*, *c/a*, and increase of *a*. This linear change of parameters can be characterised as the result of Jahn-Teller effect. The systematical change in lattice parameters and volumes indicates that Sr^{2+} is indeed doped into the bulk samples.

In order to confirm the element content of the oxide, XRF analysis was performed on $Nd_{1.2}Sr_{1.8}Mn_2O_7$ and the result shows that it has a homogeneous structure and no impurity phases such as oxides of Nd, Sr, or Mn are detected. The composition of the matrix is Nd/Sr/Mn = 1.20:1.84:1.99, which is very close to the nominal composition of 1.2:1.8:2.0.

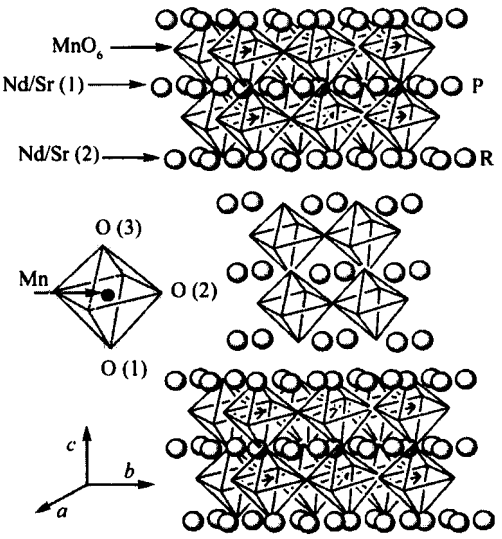

Fig. 1 Crystal structure of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$

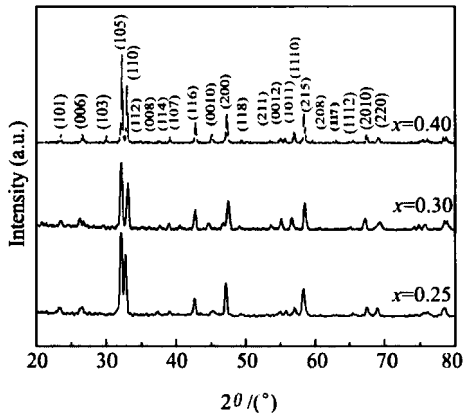

Fig. 2 XRD patterns of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.25, 0.3, 0.4$)

Table 1 Lattice constants of $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.25$, 0.3, 0.4) for different values of x

x	a/nm	c/nm	c/a	V/nm^3
0.25	0.38265	2.0312	5.30825	0.29761
0.30	0.38331	2.0257	5.28476	0.29743
0.40	0.38404	2.0083	5.22940	0.29620

The infrared absorption spectroscopy can be used to characterise the compound. Fig. 3 presents the IR spectra of the investigated compositions recorded in the range of 370 ~ 1000 cm^{-1}. The IR absorption bands of solids in the range of 100 ~ 1000 cm^{-1} are usually assigned to vibrations of ions in the crystal lattice. There are three IR-active optic modes originating from vibration and bending of metal-oxygen bonds in the infrared spectra of the pyrochlore oxides [13]. The band at about 600 cm^{-1} comes from the stretching vibration (V_s) of Mn-O in the MnO_6 octahedron and the band at about 400 cm^{-1} is assigned to the bending vibration (V_b) in the MnO_6 octahedron. In IR spectra experiments, the spectra only in the region of 370 ~