

Synthesis and Characterization of Intergrowth Type Perovskite Oxide $\text{NdSr}_2\text{MnCrO}_7$

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A new Ruddlesden-Popper phase $\text{NdSr}_2\text{MnCrO}_7$ has been prepared by the standard ceramic method. The powder X-ray diffraction studies suggest that the phase crystallizes with tetragonal unit cell in the space group $I4/mmm$. The electrical transport properties show that the phase is an electrical insulator and the electrical conduction in the phase occurs by a 3D variable range hopping mechanism. The magnetic studies suggest that the ferromagnetic interactions are dominant.

Key Words : $\text{NdSr}_2\text{MnCrO}_7$, Structure, Electric transport, Magnetic properties

Introduction

A rich variety of oxides classified as Ruddlesden-Popper (RP) phases are described as intergrowth structures having the general formula $(\text{AO})(\text{ABO}_3)_n$, where A is usually a rare-earth, alkaline-earth, or alkali ion and B can be a 3d or 4d transition-metal ion. The crystal structure of RP phases can be described by the stacking of finite n layers of perovskite ABO_3 between rock salt AO layers along the crystallographic c direction.^{1,2} The corner-sharing BO_6 octahedra form infinite sheets in the ab plane where strong electronic interactions can occur. With increasing n , anisotropic properties and an increase in dimensionality may be expected in RP phases. While the $n = 1$ member of this series (A_2BO_4) exhibits a quasi-two-dimensional K_2NiF_4 -type structure, with only one layer of corner sharing BO_6 octahedra along the c direction, the compound ABO_3 , which corresponds to the $n = \infty$ member of this series, assumes the three-dimensional distorted perovskite structure. In the second member of the RP family, $\text{A}_3\text{B}_2\text{O}_7$, two infinite BO_6 sheets are connected in the c direction between the rock-salt layers. The physical properties of various members within a given series are governed primarily by the identity and valence of the transition-metal ion, the width n of the ABO_3 perovskite slabs, the B-O-B bond angle and the oxygen content. For example, LaNiO_3 ($n = \infty$) is metallic, whereas GdNiO_3 is antiferromagnetic semiconductor as a result of decrease in Ni-O-Ni bond angle with decreasing size of the lanthanide ion. La_2NiO_4 , in which corner-sharing NiO_6 octahedral units in the ab plane are sandwiched between the LaO rock-salt layers, is semiconducting below 500 K. The electrical resistivities of the intermediate members decrease with n .³⁻⁵

A number of $n = 2$ members of RP rare earth lanthanum manganites and their substituted analogues have been reported in the literature.⁶⁻¹² Although there are many systematic studies on the hole-doped lanthanum manganites in which the concentration of the alkaline earth metal ion is varied, thereby affecting the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, which has a direct bearing on the double exchange mechanism responsible for CMR, there are far fewer studies on other rare earth

manganites and the doping at the Mn site in these systems. Notable among these are doping with various transition elements, such as Fe, Cr, Ni, Co and Ru at the Mn site. Only Ru-doped systems show enhanced FM and metallicity while the rest of the dopants destroyed the FM.¹³⁻²⁰ So it was thought interesting to synthesize a phase containing rare earth ion other than lanthanum and doped at Mn site and study its electrical and magnetic properties. The reasons to synthesise such a phase could be (i) the substitution at site B leads to tremendous variation in physical properties in many RP-phases and (ii) there are far fewer studies reported in the literature on RP-type ($n = 2$) manganites containing rare earth other than lanthanum.

In the present work, a new RP-type phase, $\text{NdSr}_2\text{MnCrO}_7$ has been synthesized and its crystal structure has been determined by powder X-ray diffractometry. The electrical resistivity and magnetic susceptibility of the phase have been studied as functions of temperature.

Experimental

$\text{NdSr}_2\text{MnCrO}_7$ polycrystalline sample was synthesized by the conventional solid state reaction method. The sample was made from starting materials MnO_2 (Aldrich 99.9%), Cr_2O_3 (Aldrich 99.9%), SrCO_3 (Aldrich 99.9%) and Nd_2O_3 (Aldrich 99.9%). Prior to use, Nd_2O_3 was heated at 1000 °C to remove moisture. The reactant oxides/carbonates were mixed in the ratio corresponding to the chemical formula of the phase with an alumina mortar and a pestle. The mixture was pressed into pellets and then heated at 1523 K with a number of intermittent grindings and pelletizings for 72 hours. Finally, the sample was cooled down slowly to room temperature in the electric furnace. The final black coloured product, after pulverization, was used for further investigations.

The total amount of various constituent cations was estimated by Perkin Elmer atomic absorption spectrometer 700. The oxygen content in the sample was determined by the oxidation-reduction method described elsewhere.^{21,22} The precise chemical composition was found to be

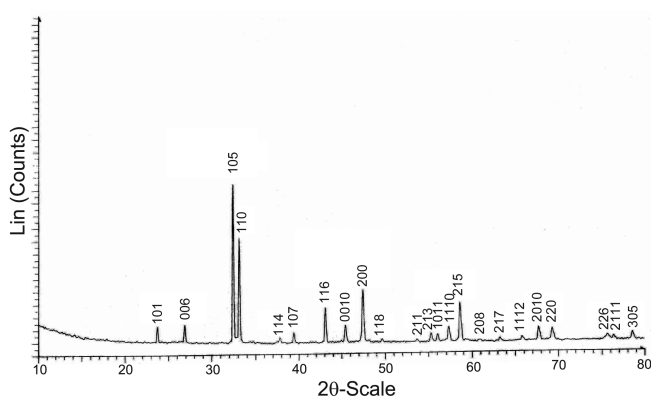
Table 1. Powder X-ray diffraction data of NdSr₂MnCrO₇ Space group: *I4/mmm* *a* = 3.8313 Å; *c* = 19.9622 Å

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{cal} (Å)	<i>I</i> _{obs}	<i>I</i> _{cal}
1	0	1	3.758	3.762	17	17
0	0	6	3.322	3.327	18	24
1	0	5	2.762	2.764	100	100
1	1	0	2.707	2.709	72	80
1	1	4	2.379	2.380	10	15
1	0	7	2.286	2.287	13	20
1	1	6	2.100	2.100	31	43
0	0	10	1.995	1.996	21	36
2	0	0	1.914	1.915	41	56
1	1	8	1.835	1.835	8	13
2	1	1	1.707	1.707	8	8
2	1	3	1.660	1.659	11	13
1	0	11	1.640	1.640	10	14
1	1	10	1.607	1.607	20	31
2	1	5	1.574	1.574	35	46
2	0	8	1.518	1.519	7	7
2	1	7	1.468	1.468	8	10
1	1	12	1.418	1.417	9	12
2	0	10	1.382	1.382	20	28
2	2	0	1.354	1.354	18	23
2	2	6	1.255	1.255	9	13
2	1	11	1.245	1.245	8	10
3	0	5	1.215	1.216	11	16

NdSr₂MnCrO_{6.94}.

The room temperature X-ray diffraction data of the phase was recorded on Bruker AXS diffractometer type D 76181 (Karlsruhe, Germany) using CuK_α radiations. The data were collected at scanning speed of 1°/minute and the 2θ range of 10–80°. The experimental XRD data is given in Table 1, while the pattern is plotted in Figure 1. Rietveld refinement of X-ray diffraction data of the phase was carried out using FULLPROF program.²³

The electrical resistivity measurements of the pellet of the product, sintered at 1400 K for about 12 hours before use, were carried out with four probe method in the temperature range 150–300 K. For the electrodes, thin copper wires were attached to the surface of the pellet with silver paste. The

**Figure 1.** X-ray diffraction pattern of NdSr₂MnCrO₇.

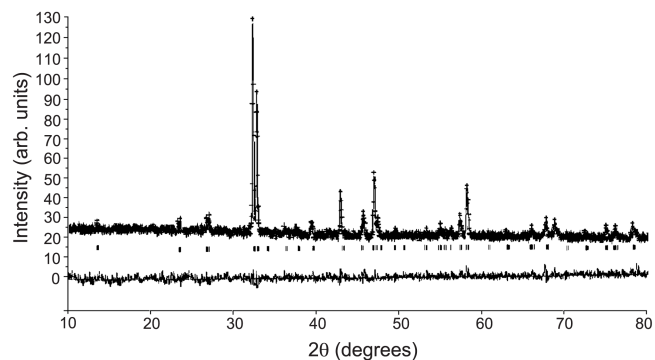
magnetic susceptibility of the polycrystalline sample was measured by means of the Faraday technique in the temperature 100–300 K using Hg[Co(SCN)₄] as calibrant in an external field of 3,700 gauss. All the magnetic susceptibility values were corrected for diamagnetism of the constituent atoms.

Results and Discussion

All the peaks of X-ray diffraction pattern of polycrystalline sample NdSr₂MnCrO₇ were successfully indexed on the tetragonal Sr₃Ti₂O₇-type structure of space group *I4/mmm*. The unit cell parameters, as refined from the program ‘Unitcell’ (method of TJB Holland and SAT Redfern 1995), are listed in the Table 1. The atomic positions of Nd/Sr, Mn/Cr and O for NdSr₂MnCrO₇ have been estimated from analogy with of Sr₃V₂O₇ without refinement.²⁴ The theoretical diffraction intensities (Table 1) of the phase were generated with programs ‘‘Diamond (Method of Klaus Brandenburg 1998) and ‘‘Mercury 2.3’’ based on the atomic positions, cell parameters and space group *I4/mmm*. The agreement between the theoretical and experimental intensities for the phase is in general satisfactory considering that the atomic positions are not refined and that, any preferred orientation effects are neglected. The XRD results confirmed that the phase with composition NdSr₂MnCrO₇ having Sr₃Ti₂O₇ type structure has been formed.

Figure 2 shows the X-ray diffraction pattern of NdSr₂MnCrO₇ and Rietveld fit to the data. The Rietveld refinement of the X-ray data was carried out to verify the phase purity. The refinements were performed using the ideal *I4/mmm* space group and the structural parameters of Sr₃Ti₂O₇ as a starting model. A pseudo-Voigt function was used for simulation of the profile of the Bragg peaks and the background was interpolated between some fixed background points of the patterns. The refinement of the structure converged with R_{wp}(%) = 16.4, R_p(%) = 21.6, R_B(%) = 4.67, R_F(%) = 3.14 and χ² = 2.62.

The temperature dependence of electrical resistivity is

**Figure 2.** Rietveld refinement pattern for NdSr₂MnCrO₇. + marks are the raw X-ray diffraction data, and the overlapped line is the calculated pattern. Vertical lines below the profile indicate the position of the allowed reflections for CuK_{α1} and CuK_{α2}. The curve at the bottom is the difference between the observed and the calculated intensities in the same scale.

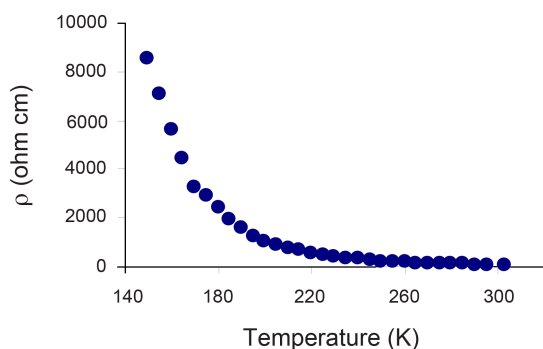


Figure 3. Plot of ρ versus Temperature (K) of $\text{NdSr}_2\text{MnCrO}_7$.

given in Figure 3, where ρ is plotted against temperature (T). The plot shows that the temperature co-efficient of resistivity is negative suggesting that the material is an insulator in the temperature range 150-300 K. The insulator behavior is attributed to the superexchange coupling of electrons. The same results were also reported earlier in such RP-type phases containing Mn and Cr ions at B site.^{25,26} Such type of manganites show insulator-metal (I-M) transition at low temperatures but our study is, however, limited to resistivity measurements in the temperature range 150-300 K. Various equations based upon different mechanisms of conduction, such as those applicable in case of Arrhenius model, polaron hopping model and variable range hopping model have been applied to the electrical resistivity data of the phase. It was observed that the equation based on 3D variable range hopping mechanism, expressed by $\rho = \rho_0 \exp(BT^{-1/4})$, was applicable to the data. The linearity of $\log \rho$ versus $T^{-1/4}$ plot (Fig. 4) in the temperature range of investigation shows that the electronic conduction occurs by a 3D variable range hopping mechanism which is generally observed in such perovskite-related phases.^{10,25,26}

The temperature dependence of the inverse molar magnetic susceptibility for $\text{NdSr}_2\text{MnCrO}_7$ is shown in Figure 5. The effective magnetic moment (μ_{eff}) has been calculated from the high temperature linear region of the χ_M^{-1} versus T plot and leads to the value 6.67 B. M. The contribution of the manganese ion (μ_{Mn}) to the magnetic moment has been calculated from the effective moment (μ_{eff}) and the theoretical magnetic moments of Nd^{3+} and Cr^{3+} ions from the relation²⁷

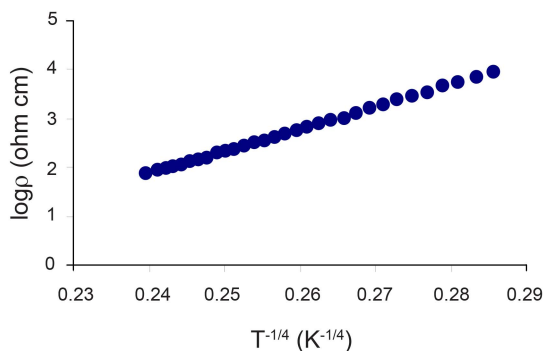


Figure 4. Plot of $\log \rho$ versus $T^{-1/4}$ of $\text{NdSr}_2\text{MnCrO}_7$.

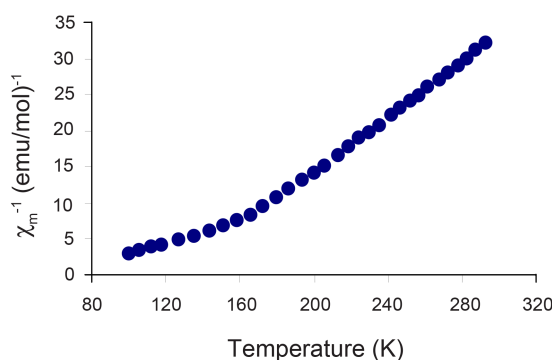


Figure 5. Plot of Inverse molar susceptibility (χ_m^{-1}) versus Temperature (K) of $\text{NdSr}_2\text{MnCrO}_7$.

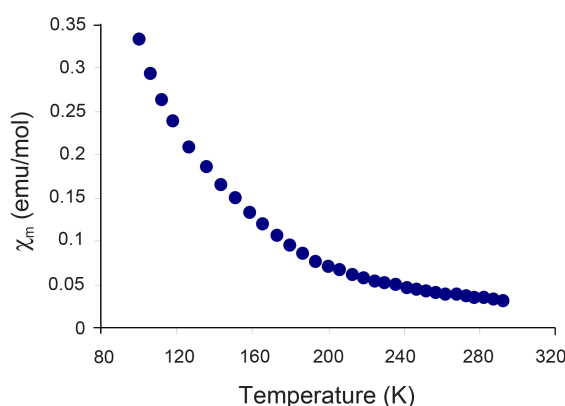


Figure 6. Plot of molar susceptibility (χ_m) versus Temperature (K) of $\text{NdSr}_2\text{MnCrO}_7$.

$$\mu_{\text{eff}}^2 = n_1 \mu_{\text{Nd}^{3+}}^2 + n_2 \mu_{\text{Mn}}^2 + n_3 \mu_{\text{Cr}^{3+}}^2$$

where n_1 , n_2 and n_3 are the number of Nd, Mn and Cr ions respectively, $\mu_{\text{Nd}^{3+}}$ is the theoretical magnetic moment of the Nd^{3+} ion (3.62 B.M) and $\mu_{\text{Cr}^{3+}}$ is that of Cr^{3+} ion, assuming it to be in the high spin state ($t_{2g}^3 e_g^0$). For μ_{Mn} , we obtain the value 4.05 B. M. This value is larger than the theoretical magnetic moment of high spin Mn^{4+} ion (3.87 B. M) which suggests that manganese ion is partly present in the 3+ oxidation state. The stoichiometry of the phase ($\text{NdSr}_2\text{MnCrO}_{6.94}$) also suggests the presence of manganese ion in mixed valence state 4+ and 3+, assuming La in 3+, Sr in 2+ and Cr in 3+ oxidation states. The Weiss constant (θ) obtained from the high temperature linear region of the χ_M^{-1} versus T plot (Fig. 5) is 120 K. The positive θ value suggests that ferromagnetic interactions are dominant in the magnetic structure of $\text{NdSr}_2\text{MnCrO}_7$. The same results were also reported earlier in such type of manganites.^{24,25} The Ferromagnetic Curie temperature (T_c), obtained from the molar magnetic susceptibility (χ_M) versus Temperature plot (Fig. 6), was found to be 140 K.

The ferromagnetic interactions could be due to double exchange (DE) interaction between Mn^{3+} and Mn^{4+} ions. Since the Cr^{3+} ion has the same electronic configuration ($t_{2g}^3 e_g^0$) as the Mn^{4+} ion, there may exist a ferromagnetic DE interaction between Cr^{3+} and Mn^{3+} ions just as between

Mn⁴⁺ and Mn³⁺ ions. The proposal has been proved by some experimental results.²⁸

Conclusions

A new RP-type phase of composition NdSr₂MnCrO₇ has been synthesized by standard ceramic method. Its structure has been determined by X-ray diffractometry. The results show that the phase crystallize in the *I4/mmm* space group with tetragonal unit cell. The electrical resistivity studies show that the material is an electrical insulator and conduction occurs by a variable range hopping mechanism. The magnetic studies suggest that the ferromagnetic interactions are dominant and manganese ion in the phase is present in mixed valence state (Mn³⁺/Mn⁴⁺).

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