

Preparation and study of structural, electrical and magnetic properties of $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$

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Abstract. Ruddlesden–Popper type phases $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$ have been prepared by traditional ceramic method and their crystal structure has been determined by powder X-ray diffraction study. The iron compound has a tetragonal unit cell with $a = 3.916 \text{ \AA}$ and $c = 20.463 \text{ \AA}$, while the phase containing manganese has $a = 3.868 \text{ \AA}$ and $c = 20.205 \text{ \AA}$ in the space group $I4/mmm$. $\text{La}_2\text{SrMn}_2\text{O}_7$ is ferromagnetic in the temperature 77–300 K and exhibits spin state transition above 210 K, while $\text{La}_2\text{SrFe}_2\text{O}_7$ is antiferromagnetic. Both the phases are insulators and electrical conduction in $\text{La}_2\text{SrMn}_2\text{O}_7$ is a function of transition in magnetic behaviour of the metal ion Mn^{3+} , while insulator behaviour is more pronounced in $\text{La}_2\text{SrFe}_2\text{O}_7$.

Keywords. $\text{La}_2\text{SrFe}_2\text{O}_7$; $\text{La}_2\text{SrMn}_2\text{O}_7$; structure, magnetic and electric transport properties.

1. Introduction

Several compounds of the composition $\text{Ln}_n\text{SrM}_n\text{O}_{3n+1}$ (Ln = rare earth ion, M = transition metal ion and $n = 1, 2, 3 \dots$) described as intergrowth phases have been reported in the literature (Joubert *et al* 1970; Fava *et al* 1972; Demazeau *et al* 1976; Benabad *et al* 1977; Rao *et al* 1988). Structurally, these phases are similar to Ruddlesden–Popper family of compounds where n perovskite layers are stacked between rock-salt layers along c -axis and the physical properties of these phases are functions of a number of parameters such as the spin state of the metal ion, oxygen content and the width of the perovskite slabs. Study of such systems gains significance because a strict comparison of physical properties of different members of a series, showing transformation of two to three dimensional structures, would be possible as the same oxidation state of the transition metal ion is maintained.

In the series $\text{La}_n\text{SrFe}_n\text{O}_{3n+1}$ and $\text{La}_n\text{SrMn}_n\text{O}_{3n+1}$ some members ($n = 1$ and 2) are reported in the literature and crystal structure, electric transport and magnetic properties of some of these phases have been studied (Joubert *et al* 1970; Benabad *et al* 1977; Cheruy and Joubert 1981; Rao *et al* 1988). LaSrFeO_4 and LaSrMnO_4 are known to possess K_2NiF_4 type structure with tetragonal unit cell, while the corresponding $n = 2$ members have crystal structure with double-perovskite slabs stacked along c -axis. John–Teller distortion of the $\text{Mn}^{\text{III}}\text{O}_6$ octahedral sites is reported in the $n = 2$ member containing manganese ion. LaSrFeO_4 is known to be antiferromagnetic with

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Fe^{3+} ion in high spin state and insulator in electric transport character. The present paper deals with preparation of $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$ by ceramic method, their characterization by powder X-ray diffractometry and study of their electric transport and magnetic properties as functions of temperature, below ambient temperature.

2. Experimental

$\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$ were prepared by the standard ceramic technique. Powders of La_2O_3 (Aldrich, 99.99%), SrO (John Mathey, 99.9%), MnO_2 (Aldrich, 99.99%) and Fe_2O_3 (J. T. Baker, 99.9%) were weighed in the appropriate proportions, carefully mixed, pressed into pellets and heated at 1573 K and 1623 K respectively for at least 48 h with several intermediate grindings and pelletizings. The heat-treatment was done in continuous flow of dry and oxygen free nitrogen, and dry oxygen for manganese and iron compounds respectively. All the reactant oxides were taken in their stoichiometric ratio, while excess SrO was added to compensate for its loss at high temperatures.

Room temperature X-ray diffraction data were recorded on Philips PW 1050/71 diffractometer with Nickel-filtered CuK_α radiations. The data were collected at scanning speed of $1^\circ/\text{minute}$. Sr/Fe and Sr/Mn ratio was estimated by Perkin Elmer atomic absorption spectrometer 3100. Oxygen content in both the samples was determined by the iodometric methods described elsewhere (Alder 1994 and Toguchi *et al* 1988). These estimations showed that within experimental error the oxides were stoichiometric $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_{7.05}$.

The electrical resistivity of pellets of the materials sintered at 1473 K for 6 h before use was recorded by four-probe method in the temperature range 30–300 K using Leybold closed cycle helium cryostat and Keithley constant current source 224 and nanovoltmeter 181. The copper wires were attached to the surface of the pellets with silver paste for the purpose of electrodes. Electrical resistivity of the samples has also been determined between 300–500 K by two-probe method. Magnetic susceptibility of the polycrystalline samples was measured by Faraday technique in the temperature range 77–300 K using $\text{HgCo}(\text{SCN})_4$ as calibrant in an external magnetic field of 3,700 gauss. All magnetic susceptibility values were corrected for diamagnetism of the constituent atoms.

3. Results and discussion

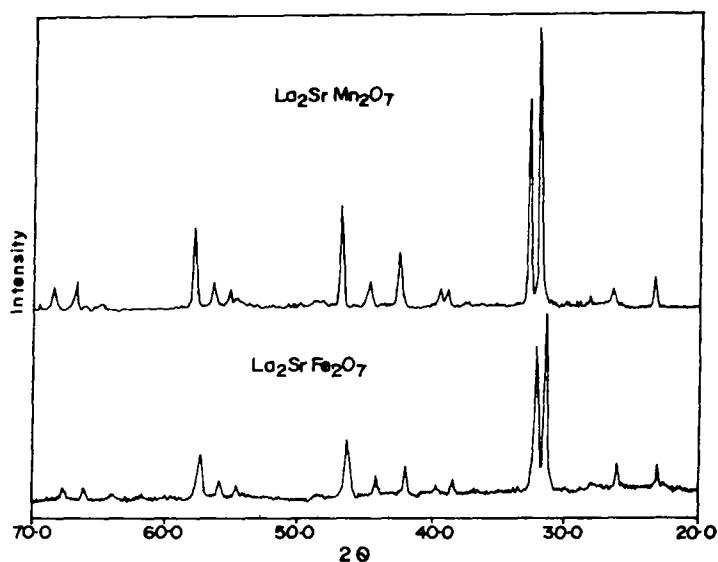
The X-ray diffraction data for $\text{La}_2\text{SrFe}_2\text{O}_7$ (table 1) could be indexed on the basis of tetragonal unit cell with $a = 3.916 \text{ \AA}$ and $c = 20.463 \text{ \AA}$ (space group $I4/mmm$), while $\text{La}_2\text{SrMn}_2\text{O}_7$ has tetragonal unit cell parameters; $a = 3.868 \text{ \AA}$ and $c = 20.205 \text{ \AA}$. No impurity of either constituent oxides was detected within the detection limit in the order of 1–2 vol% in the X-ray diffraction patterns of both the samples (figure 1). The X-ray diffraction data for $\text{La}_2\text{SrMn}_2\text{O}_7$ are given in table 2. The estimates of Sr/Fe and Sr/Mn ratio, estimation of oxygen content and the X-ray diffraction data confirm the formation of $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_{7.05}$. It may be noted that the unit cell volume shrinks while going from the iron compound to the one containing manganese.

The Lazy-Pulverix program has been used to generate the theoretical diffraction patterns of $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$ in the space group $I4/mmm$ and the atomic

Table 1. Powder X-ray diffraction data of $\text{La}_2\text{SrFe}_2\text{O}_7$ (space group $I4/mmm$)

h	k	l	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$	I_{obs}	I_{cal}
1	0	1	3.847	3.846	29	30
0	0	6	3.409	3.410	27	13
1	0	5	2.829	2.829	100	100
1	1	0	2.769	2.769	78	56
1	0	7	2.343	2.343	20	2
1	1	6	2.148	2.149	29	27
0	0	10	2.047	2.046	22	12
2	0	0	1.957	1.958	38	30
2	1	3	1.695	1.696	15	3
1	0	11	1.680	1.680	20	12
1	1	10	1.646	1.646	22	19
2	1	5	1.608	1.610	30	42
2	0	10	1.415	1.415	7	16
2	2	0	1.385	1.384	5	11

$$a = 3.916 \text{ \AA}; c = 20.463 \text{ \AA}$$

**Figure 1.** X-ray powder patterns of $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$

positions are given in tables 3 and 4. Comparison of the experimental intensities of the XRD lines and the theoretical intensities, generated with the above suggested model, shows good agreement considering that any preferred orientation effects are neglected.

The temperature dependence of the inverse molar magnetic susceptibility for $\text{La}_2\text{SrMn}_2\text{O}_7$ is shown in figure 2. It can be seen from figure 2 that an inflection is observed in the plot at around 210 K although it is not sharply defined. Above the inflection temperature, if the temperature range between 225 and 300 K is taken for a linear regression the effective moment μ_{eff} of 7.78 B. M. is observed for the sample.

Table 2. Powder X-ray diffraction data of $\text{La}_2\text{SrMn}_2\text{O}_7$ (space group $I4/mmm$)

<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$	I_{obs}	I_{cal}
1	0	1	3.794	3.799	20	32
1	0	3	3.353	3.354	13	7
1	0	5	2.791	2.794	100	100
1	1	0	2.731	2.735	77	56
1	0	7	2.310	2.313	15	1
1	1	6	2.121	2.123	26	27
0	0	10	2.020	2.021	17	12
2	0	0	1.931	1.933	41	29
2	0	4	1.804	1.806	11	1
2	1	1	1.720	1.723	12	8
1	0	11	1.660	1.659	13	12
1	1	10	1.625	1.625	17	19
2	1	5	1.590	1.590	36	42
2	0	10	1.397	1.397	17	17
2	2	0	1.367	1.367	16	11
2	2	2	1.356	1.355	11	1

$$a = 3.868 \text{ \AA}; c = 20.205 \text{ \AA}$$

Table 3. Positional co-ordinates of La, Sr, Fe and O in $\text{La}_2\text{SrFe}_2\text{O}_7$ (space group $I4/mmm$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
La, Sr (1)	0	0	0.5
La, Sr (2)	0	0	0.312
Fe	0	0	0.0965
O (1)	0	0	0
O (2)	0	0	0.189
O (3)	0	0.5	0.089

Table 4. Positional co-ordinates of La, Sr, Mn and O in $\text{La}_2\text{SrMn}_2\text{O}_7$ (space group $I4/mmm$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
La, Sr (1)	0	0	0.5
La, Sr (2)	0	0	0.312
Mn	0	0	0.097
O (1)	0	0	0
O (2)	0	0	0.189
O (3)	0	0.5	0.093

The paramagnetic Curie temperature (θ) for the high temperature linear region, given in table 5, is positive. The calculated magnetic moment for the phase from the relation ($\mu_{\text{cal}} = (2(\mu_{\text{Mn}})^2)^{1/2}$; where μ_{Mn} is the spin only magnetic moment for the high spin Mn^{3+} ion, $t_{2g}^3 e_g^1$) comes to 6.93 B. M. The μ_{eff} value is larger than the calculated magnetic

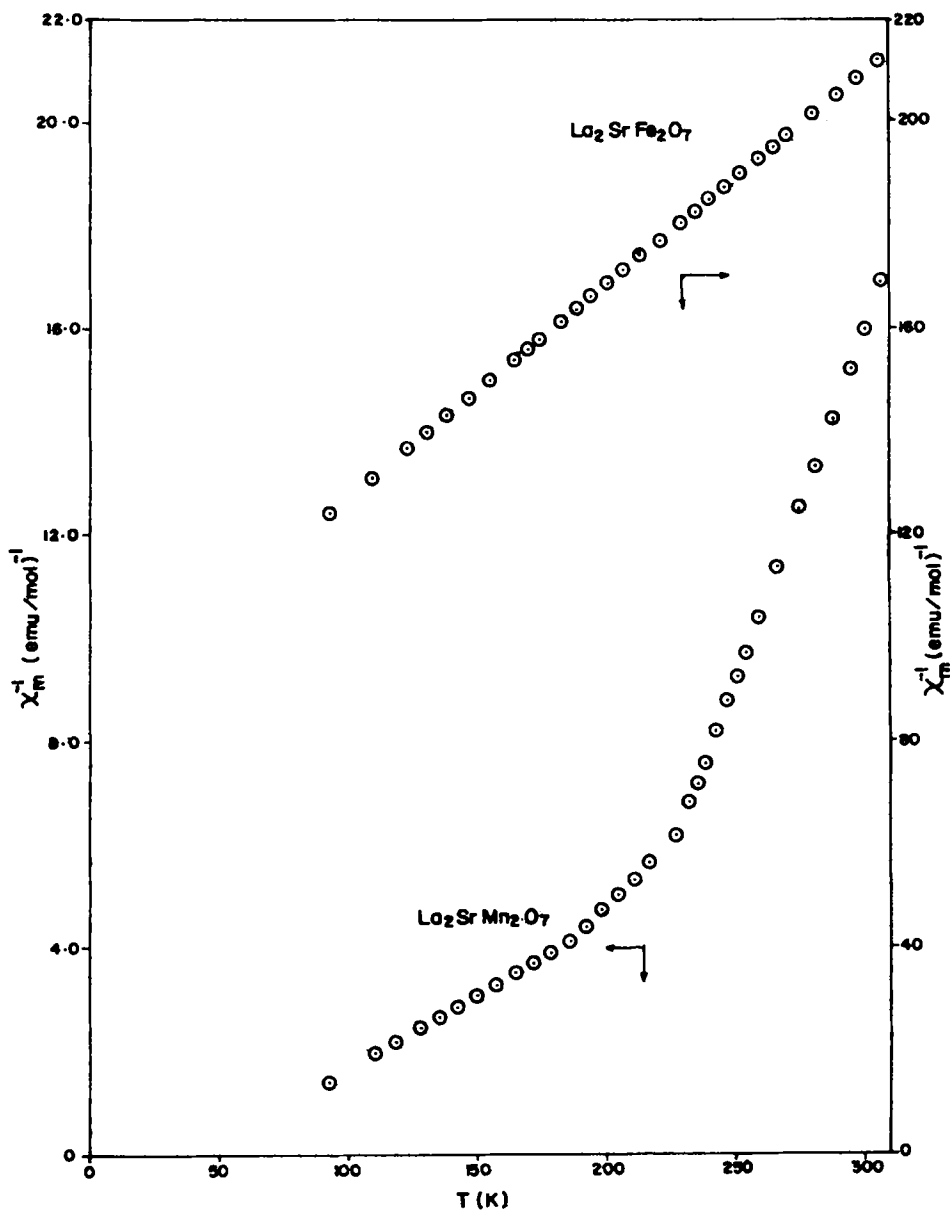


Figure 2. Temperature dependence of inverse susceptibility for $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$.

moment. The large μ_{eff} and positive θ value suggest that ferromagnetic interactions are dominant in the magnetic structure of $\text{La}_2\text{SrMn}_2\text{O}_7$. In such low dimensional system with certainly large exchange integrals between magnetic ions true paramagnetic detection is possible only at high temperature and it seems that in the present case the temperature region lies above the inflection point observed in the molar magnetic susceptibility versus temperature plot.

The iodometric analysis suggests part presence of Mn^{4+} ion in the manganese containing phase, which predominantly contains manganese ion in 3 + oxidation state. Mn-O-Mn interactions should be antiferromagnetic or weakly ferromagnetic, depending upon the Mn-O-Mn angle. In the present case the weaker ferromagnetic interactions are observed to dominate at least in the presence of an applied field. The possible reasons for this could be: (1) deviation from linearity in the Mn-O-Mn bonds as a result of John-Teller distortion and (2) introduction of Mn^{4+} ion into the $Mn^{3+} - O$ array of the lattice.

Plot of χ_m^{-1} (inverse molar magnetic susceptibility) vs T for $La_2SrFe_2O_7$ is given in figure 2. Paramagnetic Curie temperature (θ) is negative in this case (table 5), which suggests that magnetic interactions are antiferromagnetic in this case. No magnetic ordering is, however, observed in this temperature range. The effective magnetic moment (μ_{eff}) as calculated from the slope of the χ_m^{-1} vs T plot comes out to be 4.50 B. M. The decrease in the μ_{eff} value as compared to the spin only μ_{cal} value (5.91 B. M.) expected for d^5 high spin configuration ($t_{2g}^3 e_g^2$) for Fe^{3+} ion is attributed to antiferromagnetic interactions. $LaSrFeO_4$ is reported to be antiferromagnetic with Fe^{3+} ion in high spin state (Rao *et al* 1988) while perovskite $LaFeO_3$ also exhibits similar spin state behaviour. $La_2SrFe_2O_7$ could be considered as intermediate between the two phases and Fe^{3+} ion in this case is also expected to be in high spin state, which is supported by the experimental results.

The reciprocal temperature dependence of electrical resistivity ($\log \rho$) for $La_2SrMn_2O_7$ and $La_2SrFe_2O_7$ is plotted in figure 3. Both the phases have negative temperature co-efficient of resistivity (TCR), suggesting that the materials are insulators. An anomaly each in the linearity of the Arrhenius plots of $La_2SrMn_2O_7$ and $La_2SrFe_2O_7$ is observed. Corresponding to the anomaly in the slope of the Arrhenius plot for $La_2SrMn_2O_7$, the χ_m^{-1} vs T plot for the phase also shows an inflection, which is attributed to transformation in the magnetic behaviour of the material. This indicates that electrical conduction is coupled with the transition in the magnetic behaviour of the metal ion Mn^{3+} . Difference in the transition temperatures in the two studies is attributed to extrinsic factors.

As far as the anomaly in the $\log \rho$ vs $1/T$ plot for $La_2SrFe_2O_7$ is concerned, no corresponding change in the χ_m^{-1} vs T plot has been observed, which suggests that electrical conduction in this phase is not a function of spin state of the transition metal ion Fe^{3+} . The energy of activation for conduction defined by $\rho = \rho_0 \exp(-E_a/kT)$ has been estimated from the Arrhenius plots in the temperature region 300–500 K for both

Table 5. Magnetic susceptibility and electrical resistivity data^a of $La_2SrFe_2O_7$ and $La_2SrMn_2O_7$

Compound	μ_{eff} (B. M.)	θ (K)	E_a (eV)
$La_2SrFe_2O_7$	4.50	-210	0.30 (300–500 K)
$La_2SrMn_2O_7$	7.78 (225–300 K)	182 (225–300 K)	0.16 (300–500 K)

^aThe temperature region in which particular value of μ_{eff} or E_a is valid is given in parentheses.

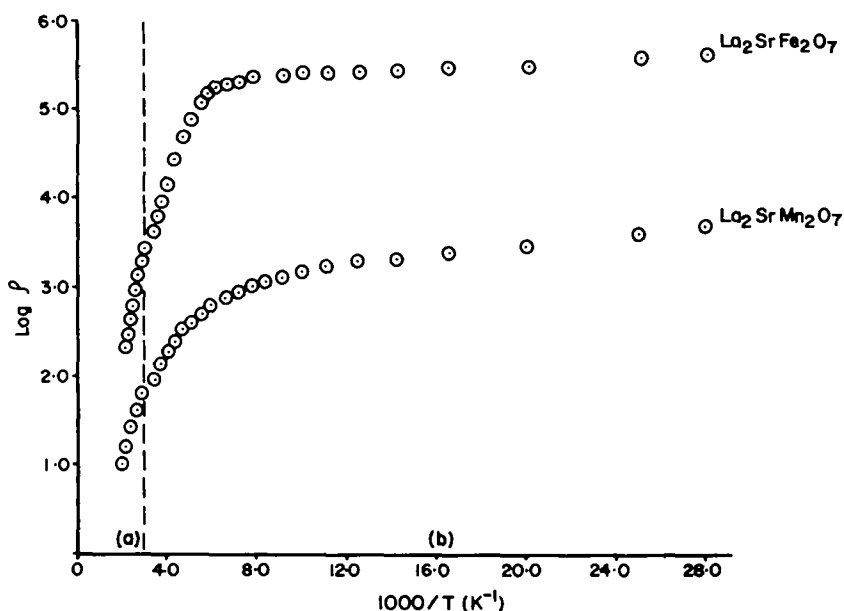


Figure 3. Inverse temperature dependence of $\log \rho$ for $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{La}_2\text{SrMn}_2\text{O}_7$: (a) four-probe method; (b) two-probe method.

the phases and the values are given in table 5. Comparison of these values suggests that the insulator behaviour is more pronounced in $\text{La}_2\text{SrFe}_2\text{O}_7$.

It is reported that the room temperature resistivity decreases as one moves from two to three-dimensional structure in Ruddlesden–Popper type of compounds (Rao *et al* 1988; Abruckle *et al* 1990). However, a comparison of the reported electrical resistivity data for two-dimensional phases with near LaSrFeO_4 stoichiometry and our results for $\text{La}_2\text{SrFe}_2\text{O}_7$ do not support this idea. Electrical resistivity is a function of many parameters such as grain size, porosity of pellets etc. and further comment on this discrepancy must await precise studies on samples in single crystal form.

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