Synthesis and characterization of Ruddlesden–Popper (RP) type phase LaSr$_2$MnCrO$_7$

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Abstract. New Ruddlesden–Popper (RP) type phase LaSr$_2$MnCrO$_7$ has been synthesized by ceramic method. Rietveld profile analysis shows that the phase crystallizes with tetragonal unit cell in the space group I4/mmm. The electrical resistivity of the phase has been measured in the temperature range of 10–300 K using Leybold closed cycle helium cryostat. The phase shows insulator–metal (I–M) transition at low temperature, the phenomenon often associated with giant magnetoresistance. 3D variable range hopping governs the electrical conduction in the insulator region above the I–M transition temperature. Magnetic susceptibility of the phase has been measured in the temperature range of 100–300 K. Magnetic studies suggest that the phase is ferromagnetic.

Keywords. LaSr$_2$MnCrO$_7$; structure; rietveld XRD analysis; magnetoresistance; ferromagnetic.

1. Introduction

The Ruddlesden–Popper (RP) type phases of general formula A$_{n+1}$B$_n$O$_{3n+1}$ or AO(ABO$_3$)$_n$ (where A is rare earth/alkaline earth ion, B is a transition metal ion), generally crystallize with tetragonal or orthorhombic unit cell in the space group *I4/mmm* or *Fmmm*.[1–7] The crystal structure of these phases can be described by the stacking of finite *n* layers of perovskites ABO$_3$ between rock salt AO layers along the crystallographic *c* direction.[8] The first member of the RP family, *n* = 1, is A$_2$BO$_4$, which adopts the K$_2$NiF$_4$-type structure with only one layer of corner-sharing BO$_6$ octahedra along the *c* direction. In the second member of the RP family, A$_3$B$_2$O$_7$, two infinite BO$_6$ sheets are connected in the *c* direction between the rock-salt layers. The three ABO$_3$ perovskite layers with corner-sharing BO$_6$ octahedra along *c* direction are separated by AO rock-salt layers in the third member of the RP family, A$_4$B$_3$O$_{10}$. The *n* = 1 phases with K$_2$NiF$_4$ type structure, possess 2D character. Increase in *n* is expected to strengthen B–O–B interactions along the crystallographic *c*-axis resulting in increased 3D character in higher members of the family. Physical properties of such phases are governed by valence state of ions, width of *n* perovskite slabs and oxygen content. These phases are generally electrical insulators and antiferromagnetic in nature, although some exceptions from this general trend has also been observed.[9–11] The substitution at A and B sites show many interesting physical properties. Some layered manganites with RP-type structure (*n* = 2) are known to exhibit insulator–metal (I–M) transition in their electric transport behaviour and ferromagnetic transformation at low temperatures, the phenomenon associated with giant magnetoresistance.[12,13]

Some Cr doped LaSr$_2$Mn$_2$O$_7$ manganites with layered structure are reported in the literature.[14,15] The increase of resistivity and slight change in magnetization in these phases is related to the combined effect of the partial destruction of the Mn–O–Mn interaction network within the ferromagnetic (FM) layers of an A-type antiferromagnet and the appearance of Cr^{3+}–O–Mn^{3+} FM interaction. Additionally, the introduction of the random Coulomb potential caused by the substitution of Cr^{3+} for Mn^{3+} is also a source of increased resistivity. The electrical conduction in such phases is governed by three-dimensional variable range-hopping (VRH) mechanism. In this paper, the new RP-type phase LaSr$_2$MnCrO$_7$ has been synthesized and its crystal structure has been determined by Rietveld profile analysis of X-ray diffraction data. The electrical resistivity and magnetic susceptibility has been studied as functions of temperature.

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2. Experimental

The phase $LaSr_2MnCrO_7$ was prepared by the standard ceramic method by heating the stoichiometric amounts of La_2O_3, $SrCO_3$, Mn_2O_3 and Cr_2O_3 (purity 99·9%). A 5% of $SrCO_3$ was added in excess to compensate for its loss at high temperature. Prior to use, La_2O_3 was heated at 950°C to remove absorbed moisture and CO_2. Before heating, the reactants were mixed and homogenized by grinding in cyclohexane and pressed into pellets. The pellets were heat-treated at 1543 K in static air atmosphere for about 90 h with a number of intermediate grindings and pelletizings. The black coloured products were finally pulverized and analysed by usual chemical methods for the constituent cations.

Room temperature powder X-ray diffraction data of the phase was recorded on Phillips diffractometer type PW 1820 using CuK_α radiations in 2θ range of 10–70°. The data were analysed with the Rietveld analysis programme DBWS-9807 for the structure determination.[16]

The electrical resistivity of the pellet of the phase sintered at 1450 K was recorded by four probe method in the temperature range of 10–300 K using Leybold closed cycle helium cryostat. Thin copper wires were attached to the surface of pellet with Epotek silver epoxy E-4110 for the purpose of electrodes. The magnetic susceptibility of the polycrystalline phase was measured by Faraday technique in the temperature of range 100–300 K using $Hg[Co(SCN)_4]$ as calibrant. All magnetic susceptibility values were corrected for diamagnetism of the constituent ions.

3. Results and discussion

The X-ray diffraction data of $LaSr_2MnCrO_7$ could be indexed with tetragonal unit cell in the space group *I4/mmm*. No trace of any extra peaks due to constituent oxides or $n = 1$ or $n = 3$ phases was found, suggesting the formation of single phase compound. The Rietveld analysis of the X-ray diffraction data of the phase was done starting with the model of the well-known RP-type $n = 2$ phase, $Sr_3Ti_2O_7$.[8] The structure was refined in the space group *I4/mmm*, assuming a pseudo-Voight (pV) peak shape function. The Rietveld refinement of the powder diffraction data is shown in figure 1. The refinement values, structural parameters and *R*-factors along with the estimated standard deviation (ESD) of the last signi-

ficant number for the phase are given in the table 1. The S (goodness of fit) value calculated from R_{wb}/R_{exp} comes to be 1·28. The selected bond lengths and bond angles, calculated from the structural parameters of the phase, are also tabulated in the table 1. The results suggest that the occupancy of oxygen at the site (2a; 0 0 0) is 0·95, which shows that the phase is oxygen deficient with composition $LaSr_2MnCrO_{7-\delta}$. It may be noted that of the three oxygen positions, the O(1) site is of course, the preferred one for the oxygen loss in this type of phases.[17] The decrease in oxygen content suggests that manganese is present in mixed valence state of Mn^{3+}/Mn^{4+}. The temperature factor (B) has comparatively large values for various ions, especially the oxygen ions, signifying displacement of the ions from their ideal positions. A look at the bond angles and the bond lengths for the phase shows that there is significant distortion in the cell structure.

The goodness of fit, S, value 1·28 for the phase is reasonable for assigning the structure to the phase on the basis of the Rietveld analysis. The results of X-ray diffraction studies show that the phase with composition $LaSr_2MnCrO_{7-\delta}$ has been formed with the RP-type ($n = 2$) structure, where unit cell takes up distorted structure due to John–Teller effect, which is caused by part presence of Mn^{3+} ion. Representative unit cell structure of $LaSr_2MnCrO_7$ is given (see figure 4).

The temperature dependence of resistivity of the phase is shown in figure 2. The plot shows that the temperature co-efficient of resistivity is negative, above 48 K suggesting that the material is an insulator above this temperature. The linearity of log ρ versus $T^{-1/4}$ plot (figure 2) in the temperature region (70–300 K) shows that the electronic conduction in the insulator region occurs by a 3D variable range hopping mechanism. The insulator behaviour is attributed to the superexchange coupling of electrons. As the temperature falls below 48 K, the temperature coefficient of resistivity abruptly becomes positive and the phase becomes metallic in nature. It is reported in the literature that mixed valence layered manganites exhibit I–M transition at low temperatures and the Mn^{3+}/Mn^{4+} mixed valence state in these manganites creates mobile charge carriers which is for I–M transition.[12,13,18,19]. The I–M transition is due to transfer of e_g electron between Mn^{3+} and Mn^{4+} oxidation states by double exchange mechanism. The ionic states (Mn^{3+}/Mn^{4+}) fluctuates because of electron transfer between them.

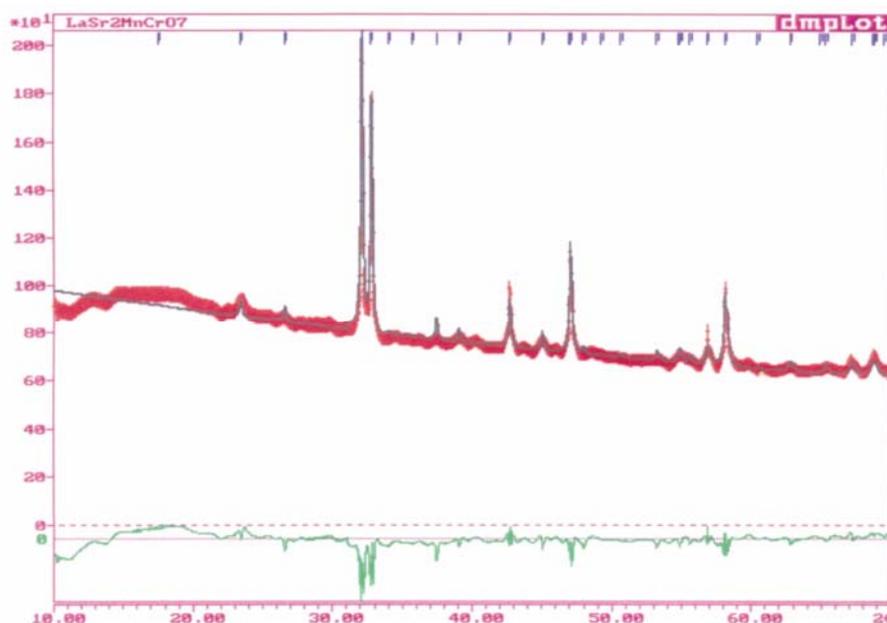**Figure 1.** Rietveld plots showing the observed, calculated and the difference pattern for $LaSr_2MnCrO_7$.

Table 1. Structural parameters of $LaSr_2MnCrO_7$.

Positional co-ordinates of La, Sr, Mn, Cr and O

Atom	Site	x	y	z	$B(\text{Å}^2)$	Occupancy
La/Sr(1)	2b	0·0	0·0	0·5	0·98(2)	1
La/Sr(2)	4e	0·0	0·0	0·3116(6)	0·92(5)	1
Mn/Cr	4e	0·0	0·0	0·0910(5)	1·03(4)	1
O(1)	2a	0·0	0·0	0·0	1·36(10)	0·95(4)
O(2)	4e	0·0	0·0	0·1749(9)	1·32(7)	1
O(3)	8g	0·0	0·5	0·1083(7)	1·12(5)	1

Selected bond lengths (Å)

La/Sr(1)–Sr(2)	3·781 (0·004)
La/Sr(2)–O(2)	2·743 (0·020)
Mn/Cr–O(1)	1·826 (0·008)
Mn/Cr–O(2)	1·684 (0·004)
Mn/Cr–O(3)	1·958 (0·021)

Selected bond angles (°)

La/Sr(1)–La/Sr(2)–O(2)	180·00 (0·26)
O(2)–Mn/Cr–O(3)	79·78 (0·62)
O(1)–Mn/Cr–O(2)	180·00 (0·50)
O(1)–Mn/Cr–O(3)	100·21 (0·49)
La/Sr(2)–O(2)–Mn/Cr	180·00 (0·66)

Lattice constants: $a = 3·8533$ (21) Å, $c = 20·0710$ (36) Å, Cell volume = 298·01 Å³, $R_{wp} = 4·53\%$, $R_{exp} = 3·54\%$ and S (goodness of fit) = 1·28.

Inverse molar magnetic susceptibility χ_M^{-1} versus temperature plot for the phase is given in figure 3. The curie temperature (θ) from the high temperature region is positive suggesting that the phase is ferro-magnetic. The variation of magnetization with temperature (figure 3) also shows ferromagnetic behaviour with temperature of ferromagnetic ordering of 134 K. The ferromagnetism arises due to Mn^{3+}–O–
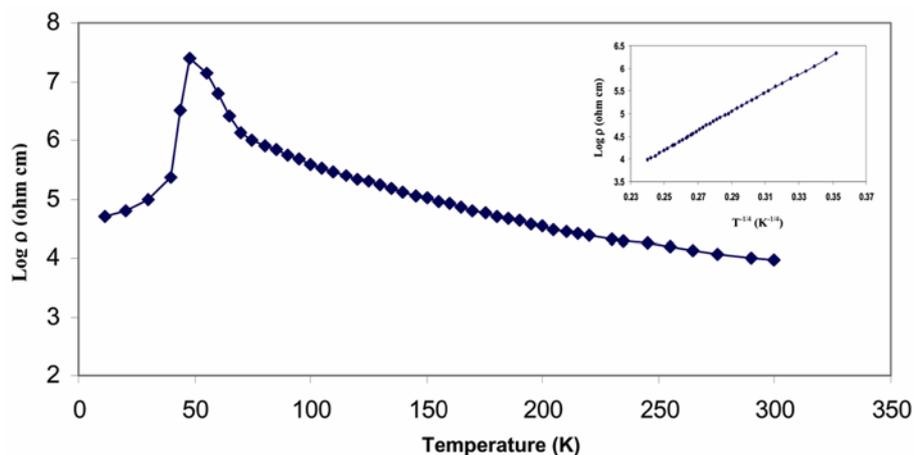
Figure 2. Plot of log ρ versus temperature (K) of LaSr$_2$MnCrO$_7$. Inset shows the log ρ versus $T^{-1/4}$ plot of LaSr$_2$MnCrO$_7$.
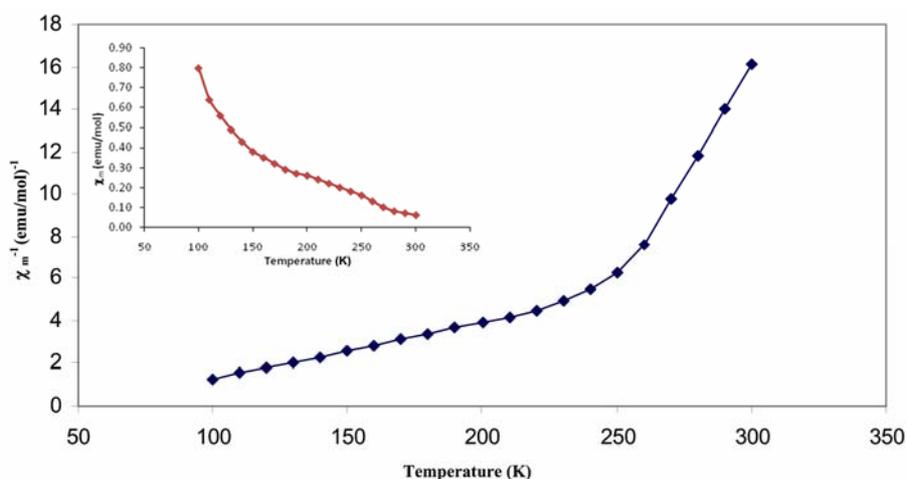

Figure 3. Plot of inverse molar susceptibility (χ_m^{-1}) versus temperature (K) of LaSr$_2$MnCrO$_7$. Inset shows the magnetization versus temperature (K) plot of LaSr$_2$MnCrO$_7$.

Mn^{4+} interactions in the *ab* plane. In addition, we note that the Cr^{3+} ion has the same electronic configuration ($t_{2g}^3 e_g^0$) as the Mn^{4+} ion when the Cr ions enter into the Mn site in the form of Cr^{3+} ions. Therefore, there may exist a FM interactions between Cr^{3+} and Mn^{3+} ions just as between Mn^{4+} and Mn^{3+} ions. This has been proved by some experimental results.[20] The effective magnetic moment (μ_{eff}) has been calculated from the high temperature region (250–300 K) and comes to be 6·03 B.M. The contribution of manganese ion (μ_{Mn}) to the magnetic moment has been calculated from the effective magnetic moment (μ_{eff}) and theoretical magnetic moment of Cr ion from the relation[21]

$$\mu_{\text{eff}}^2 = n_1 \mu_{\text{Cr}^{3+}}^2 + n_2 \mu_{\text{Mn}^{4+}}^2,$$

where n_1 and n_2 are the number of Cr and Mn ions in the phase.

$\mu_{\text{Cr}^{3+}}$ is the theoretical magnetic moment of the Cr ion, assuming it to be in the high spin +3 oxidation state ($t_{2g}^3 e_g^0$). For μ_{Mn}, we obtain the value 4·62 B. M for the given phase. This value is higher than the theoretical magnetic moment of high spin Mn^{4+} ion (3·87 BM) which suggests that the manganese ion is partly present in +3 oxidation state. The results show that the Mn is in the mixed valence state (Mn^{3+}/Mn^{4+}), the condition essential for the I–M transition.

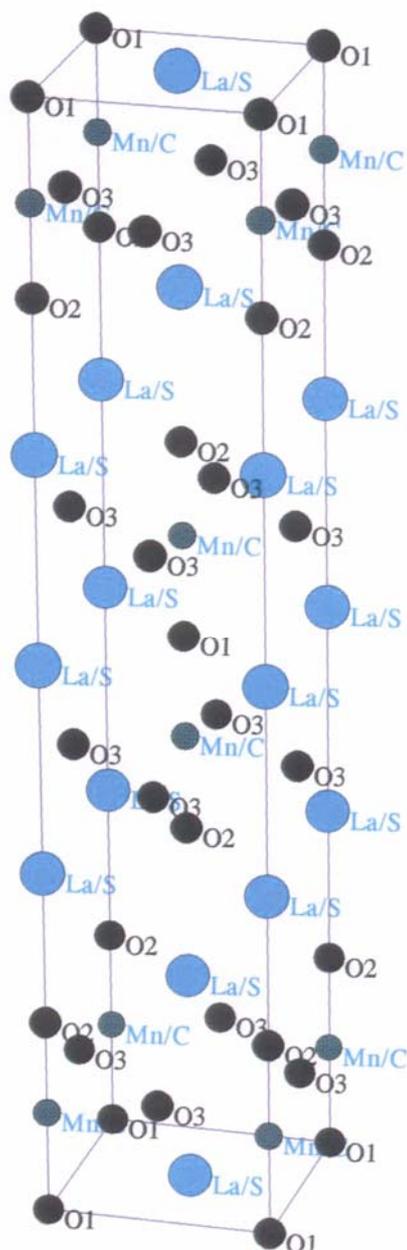**Figure 4.** Unit cell structure of LaSr₂MnCrO₇.

4. Conclusion

A new RP-type phase of composition **LaSr₂MnCrO₇** has been synthesized by standard ceramic method. Its structure has been determined by Rietveld analysis of XRD data. The results show that the phase crystallize in the *I*4/*mmm* space group with tetragonal unit cell. The electrical resistivity studies show that the material is insulator in the temperature region of 48–300 K and conduction occurs by a variable range hopping mechanism. The phase undergoes I–M transition around 48 K and this is attributed to the mixed valence Mn^{3+}/Mn^{4+} state. The magnetic studies suggest that the phase is ferromagnetic and manganese ion in the phase is present in mixed valence state (Mn^{3+}/Mn^{4+}).

References

1. Liang Z, Tang K, Shao Q, Li G., Zeng S and Zeng H 2008 *J. Solid State Chem.* **181** 964
2. Bendersky L A, Greenblatt M and Chen R 2003 *J. Solid State Chem.* **174** 418
3. Zhang Z, Greenblatt M and Goodenough J B 1994 *J. Solid State Chem.* **108** 402
4. Sreedhar K, McElfresh M, Perry D, Kim D, Metcalf P and Honig J M 1994 *J. Solid State Chem.* **110** 208
5. Rao C N R, Ganguly P, Singh K K and Mohan Ram R A 1988 *J. Solid State Chem.* **72** 14
6. Sharma I B, Singh D and Magotra S K 1998 *J. Alloys Compd.* **269** 13
7. Sharma I B and Singh D 1998 *Bull. Mater. Sci.* **21** 363
8. Ruddlesden S N and Popper P 1958 *Acta Crystallogr.* **11** 54
9. Battle P D, Bollen S K and Powell A V 1992 *J. Solid State Chem.* **99** 267
10. Attfield M P, Battle P D, Bollen S K, Kim S H, Powell A V and Worlman M J 1992 *J. Solid State Chem.* **96** 344
11. Lee J Y, Swinnea J S, Steinfink H, Reiff W M, Pei S and Jorgensen J D 1993 *J. Solid State Chem.* **103** 1
12. Mahesh R, Mahendiran R, Raychaudhuri A K and Rao C N R 1996 *J. Solid State Chem.* **122** 448
13. Briceno G. Chang H, Sun X, Schultz P G and Xiang X D 1995 *Science* **270** 273
14. Zhang R L, Zhao B C, Song W H, Ma Y Q, Yang J, Sheng Z G and Dai J M 2004 *J. Appl. Phys.* **96** 4965
15. Ang R, Zhang R L, Zhao B C, Zhu X B, Song W H and Sun Y P 2006 *Solid State Commun.* **137** 492
16. Young R A, Larson A C, Paiva C O Santos 1998 DBWS-9807 Program for Rietveld Analysis, School of Physics, Georgia Institute of Technology, Atlants
17. Dann S E, Weller M T and Curie D B 1992 *J. Solid State Chem.* **97** 179
18. Raveau B, Maignan A and Caignaert V 1995 *J. Solid State Chem.* **117** 424
19. Von Helmolt R, Wecker J, Hotzapfel B, Schultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331
20. Maignan A, Martin C, Damay F, Hervieu M and Raveau B 1998 *J. Magn. Magn. Mater.* **188** 185
21. Subramanian M A, Toradi C C, Johnson D C, Pannetier J and Sleight A W 1998 *J. Solid State Chem.* **72** 24