

Synthesis, structure and low temperature study of electric transport and magnetic properties of $\text{GdSr}_2\text{MnCrO}_7$

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Abstract. The layered perovskite oxide, $\text{GdSr}_2\text{MnCrO}_7$, 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 properties suggest that the ferromagnetic interactions are dominant in the high temperature region.

Keywords. Chemical synthesis; X-ray diffraction; electrical properties; magnetic properties.

1. Introduction

Layered perovskite oxides are a promising group of mixed-conducting materials with potential applications for oxygen-separation membranes, gas sensor devices and electrodes of intermediate-temperature solid oxide fuel cells (Moseley and Williams 1989; Meixner and Lampe 1996; Skinner and Kilner 2000; Ormerod 2003). These types of oxides with composition, $\text{La}_{2-x}\text{M}_{1+x}\text{Mn}_2\text{O}_7$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$), have attracted particular attention of researchers owing to their remarkable properties, including electronic and impurity phase separation, giant magnetoresistance, and some others (Kimura and Tokura 2000; Dagotto *et al* 2001). In general, the layered perovskite can be represented as Ruddlesden–Popper (RP) series of general formula, $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ or $\text{AO}\cdot(\text{ABO}_3)_n$, where n is the number of perovskite blocks composed of two-dimensional layers of BO_6 corner-sharing octahedra separated by rock salt AO layers (Ruddlesden and Popper 1957, 1958), A is a rare earth element and B is a transition element. A number of $n = 2$ members of RP rare earth lanthanum manganites and their substituted analogues have been reported in the literature (Jung 2000, 2003; Arbuzova *et al* 2003; Sudhakar and Rajeev 2004; Zhang *et al* 2004; Yankin *et al* 2006; Fedorova *et al* 2008). Although there are many systematic studies on the hole-doped manganites in which 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 rest of the

dopants destroyed the FM (Gundakaram *et al* 1999; Zhang *et al* 1999, 2000; Raveau *et al* 2000; Maignan *et al* 2001; Martin *et al* 2001; Sahu *et al* 2002; Sudhakar *et al* 2003).

In the present work, a new RP-type phase, $\text{GdSr}_2\text{MnCrO}_7$ 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.

2. Experimental

$\text{GdSr}_2\text{MnCrO}_7$ was prepared by the standard ceramic method by heating stoichiometric amounts of MnO_2 (Aldrich 99.9%), Cr_2O_3 (Aldrich 99.9%), Gd_2O_3 (Aldrich 99.9%), except SrCO_3 (Aldrich 99.9%), 5% of which was added in excess to compensate for its loss at high temperature. Prior to use, Gd_2O_3 was heated at 1000°C to remove moisture. Before heating, the mixtures were homogenized by grinding and pressed into pellets. The pellets were heat-treated at $1553 (\pm 10)$ K in static air for about 72 h with a number of intermittent grindings and pelletizings. Finally, the sample was cooled down slowly to room temperature in the electric furnace. The black coloured product was finally pulverized. The amount of cations in the phase was determined by quantitative analysis within an accuracy of $\sim 2\%$. The oxygen content in the sample was determined by iodometric method. The precise chemical composition was determined to be $\text{GdSr}_2\text{MnCrO}_{6.93}$.

The room temperature X-ray diffraction data of the phase was recorded on Bruker AXS diffractometer type D 76181 (Karlsruhe, Germany) using $\text{CuK}\alpha$ radiations. The data were collected at a scanning speed of $1^\circ/\text{min}$ and in the 2θ range of $10\text{--}80^\circ$. The experimental XRD data is given in table 1, while the pattern is plotted in figure 1.

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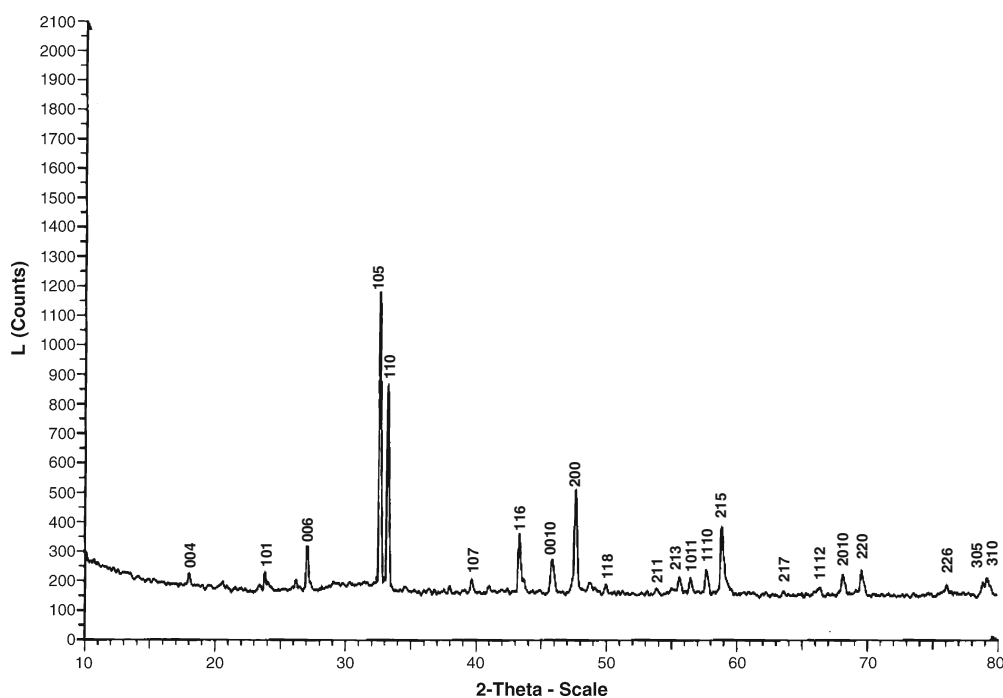


Figure 1. X-ray diffraction pattern of $\text{GdSr}_2\text{MnCrO}_7$.

The electrical resistivity measurements of the pellet of the product, sintered at 1400 K for about 12 h 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 magnetic susceptibility of the polycrystalline sample was measured by means of the Faraday technique in the temperature range 100–300 K using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant in an external field of 3,700 gauss. All the magnetic susceptibility values were corrected for diamagnetism of the constituent atoms.

3. Results and discussion

All the peaks of X-ray diffraction pattern of polycrystalline sample, $\text{GdSr}_2\text{MnCrO}_7$, were successfully indexed on the tetragonal $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type structure of space group $I4/mmm$. The unit cell parameters, refined from the program 'Unit Cell', are listed in table 1. The atomic positions of Gd, Sr, Mn, Cr and O were generated for $\text{GdSr}_2\text{MnCrO}_7$ from the known positional parameters of $\text{Sr}_3\text{V}_2\text{O}_7$ (Suzuki *et al* 1991) and are given in table 2. The theoretical diffraction intensities (table 1) of the phase were generated with a program 'Mercury' based on these 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 quantitative analysis, oxygen stoichiometry, the agreement between d_{obs} and d_{cal} and that between I_{obs} and I_{cal} values

Table 1. Powder X-ray diffraction data of $\text{GdSr}_2\text{MnCrO}_7$ (Space group: $I4/mmm$, $a = 3.8177(4)$ Å and $c = 19.7977(5)$ Å).

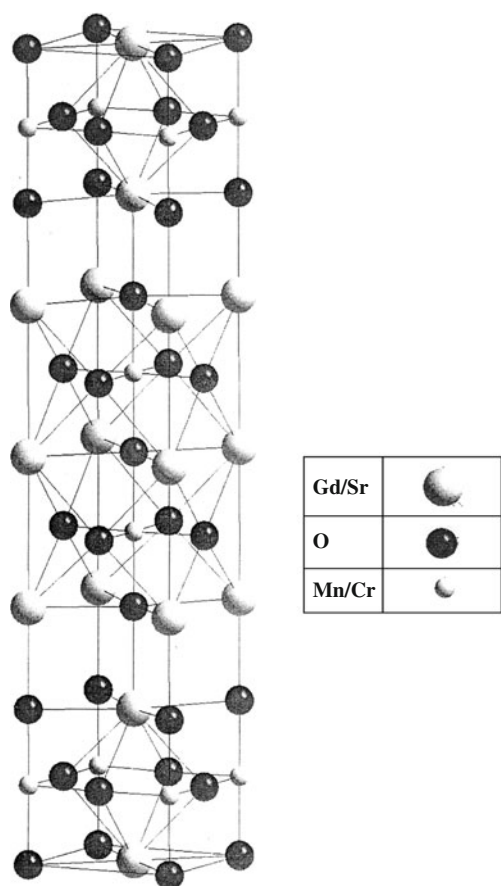
h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}
0	0	4	4.941	4.949	5	6
1	0	1	3.742	3.748	20	34
0	0	6	3.298	3.299	29	31
1	0	5	2.746	2.748	100	100
1	1	0	2.697	2.699	74	78
1	0	7	2.272	2.272	17	48
1	1	6	2.088	2.089	30	34
0	0	10	1.979	1.979	23	52
2	0	0	1.907	1.908	43	44
1	1	8	1.824	1.824	16	17
2	1	1	1.701	1.701	14	18
2	1	3	1.652	1.652	18	15
1	0	11	1.628	1.627	17	15
1	1	10	1.597	1.596	20	31
2	1	5	1.568	1.567	32	46
2	1	7	1.461	1.461	14	15
1	1	12	1.407	1.407	15	14
2	0	10	1.374	1.374	18	17
2	2	0	1.350	1.349	20	21
2	2	6	1.249	1.249	3	4
3	0	5	1.214	1.212	6	4
3	1	0	1.207	1.207	9	13

suggests that the phase with composition, $\text{GdSr}_2\text{MnCrO}_{6.93}$, having $\text{Sr}_3\text{Ti}_2\text{O}_7$ type structure has been formed.

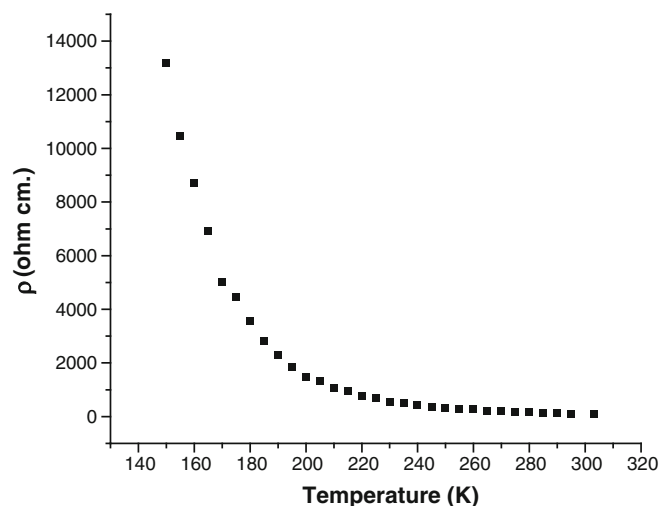
Selected interatomic bond lengths and bond angles have also been calculated from the structural parameters, which

Table 2. Structural parameters of $GdSr_2MnCrO_7$.

Atom	Site	x	y	z
Positional coordinates of Gd, Sr, Mn, Cr and O (Space group, $I4/mmm$)				
Gd/Sr (1)	2b	0.0	0.0	0.5
Gd/Sr (2)	4e	0.0	0.0	0.3148 (3)
Mn/Cr	4e	0.0	0.0	0.0971 (7)
O (1)	2a	0.0	0.0	0.0
O (2)	4e	0.0	0.0	0.190 (2)
O (3)	8g	0.0	0.5	0.096 (2)
Selected bond lengths (Å)				
Gd/Sr(2)–O(2)		2.491 (40)	Gd/Sr(2) – O(2)	2.711 (1)
Gd/Sr(2)–O(3)		2.615 (27)	Gd/Sr(2) – O(3)	2.710 (28)
Gd/Sr(2) – O(1)		2.709 (0)	Mn/Cr – O(2)	1.854 (42)
Mn/Cr – O(1)		1.938 (14)	Mn/Cr – O(3)	1.916 (0)
Bond angles (°)				
O(2) – Mn/Cr – O(3)		90.66 (105)	O(1) – Mn/Cr – O(3)	89.34 (77)
O(2) – Mn/Cr – O(1)		179.99 (86)	Gd/Sr(1) – Gd/Sr(2) – O(2)	180 (0)
Mn/Cr – O(1) – Mn/Cr		180 (34)	Mn/Cr – O(3) – Mn/Cr	178.69 (42)


Figure 2. Unit cell structure of $GdSr_2MnCrO_7$.

are tabulated in table 2. The average coordination geometry about the transition metal (Mn/Cr) site is somewhat irregular, which is often observed in the RP-type phases (Atfield


Figure 3. Plot of ρ vs temperature (K) of $GdSr_2MnCrO_7$.

et al 1992; Battle *et al* 1992). One of the reasons for this asymmetry in the present case seems to be the presence of the mixed valence state of the manganese ion (Mn^{3+}/Mn^{4+}) in the lattice. The mixed valence state of Mn could be due to the oxygen deficiency in the phase. The Mn/Cr–O(1) bond is stretched and longest of all are the Mn/Cr–O bonds in $GdSr_2MnCrO_7$. This implies that the structure has the freedom to adapt along the *c*-axis. The unit cell structure of the phase as drawn with the program ‘Diamond’ is given in figure 2.

The temperature dependence of electrical resistivity is given in figure 3, where ρ is plotted against temperature (*T*). The plot shows that the temperature coefficient of resistivity is negative suggesting that the material is an insulator in

the temperature range 150–300 K. The linearity of $\log \rho$ versus $T^{-1/4}$ plot (figure 4) in the temperature of investigation shows that the electronic conduction occurs by a 3D variable range hopping (VRH) mechanism expressed by

$$\rho = \rho_0 \exp(BT^{-1/4}).$$

The insulator behaviour is attributed to the superexchange coupling of electrons. 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.

The temperature dependence of the inverse molar magnetic susceptibility for $\text{GdSr}_2\text{MnCrO}_7$ is shown in figure 5.

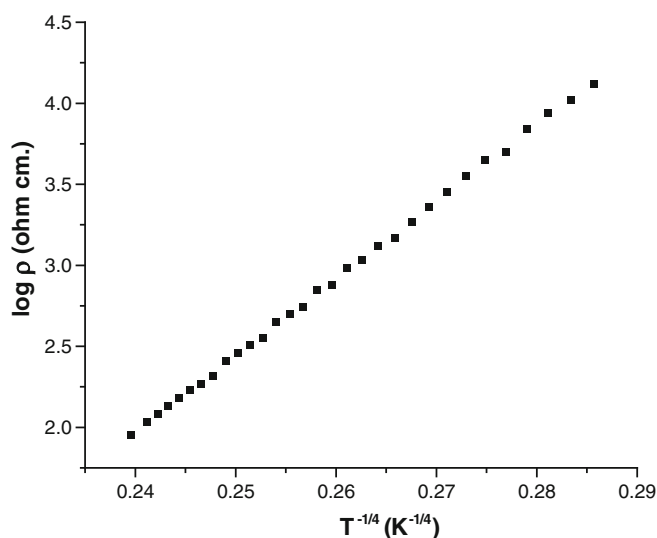


Figure 4. Plot of $\log \rho$ vs $T^{-1/4}$ of $\text{GdSr}_2\text{MnCrO}_7$.

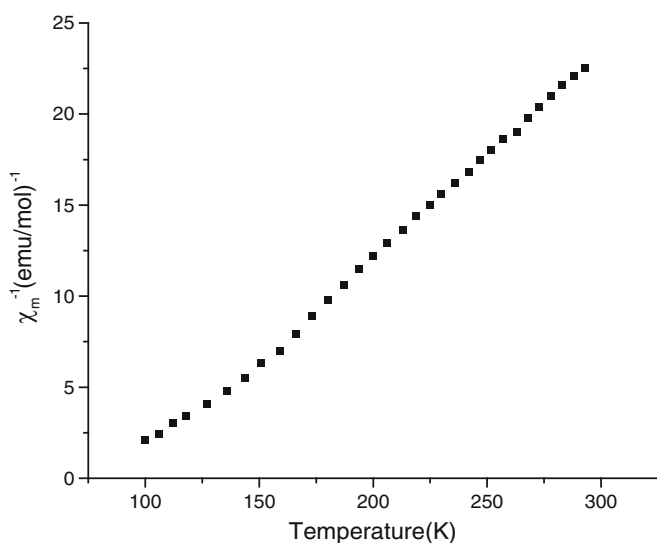


Figure 5. Plot of inverse molar susceptibility (χ_M^{-1}) vs temperature (K) of $\text{GdSr}_2\text{MnCrO}_7$.

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 a value of 9.81 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 Gd^{3+} and Cr^{3+} ions from the relation (Subramanian *et al* 1988)

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

where n_1 , n_2 and n_3 are the number of Gd, Mn and Cr ions, respectively. $\mu_{\text{Gd}^{3+}}$ is the theoretical magnetic moment of the Gd^{3+} ion (7.94 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 a value of 4.26 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 3+ oxidation state. The stoichiometry of the phase ($\text{GdSr}_2\text{MnCrO}_{6.93}$) also suggests the presence of manganese ion in mixed valence state 4+ and 3+ (93:7 by %), assuming La in 3+, Sr in 2+ and Cr in 3+ oxidation states. It has been observed from the χ_M^{-1} vs T plot (figure 5) that the Weiss constant (θ) obtained from the high temperature linear region is 56 K. The positive (θ) value suggests that ferromagnetic interactions are dominant in the magnetic structure of $\text{GdSr}_2\text{MnCrO}_7$. The ferromagnetic curie temperature (T_c) obtained from the molar magnetic susceptibility (χ_M) vs temperature plot 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 Mn^{4+} and Mn^{3+} ions. The proposal has been proved by some experimental results (Maignan *et al* 1998).

4. Conclusions

A new RP-type phase of composition, $\text{GdSr}_2\text{MnCrO}_7$, has been synthesized by standard ceramic method. Its structure has been determined by X-ray diffractometry. The results show that the phase crystallizes 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 ($\text{Mn}^{3+}/\text{Mn}^{4+}$).

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References

- Arbuzova T I, Naumov S V and Arbuzov V L 2003 *Phys. Solid State* **45** 1513
- Attfield M P, Battle P D, Bollen S K, Kin S H, Powell A V and Worlman M 1992 *J. Solid State Chem.* **96** 344
- Battle P D, Bollen S K and Powell A V 1992 *J. Solid State Chem.* **99** 267
- Dagotto E, Hotta T and Moreo A 2001 *Phys. Rep.* **344** 1
- Fedorova M O, Yankin A M, Zvereva I A, Titova S G and Balakirev V F 2008 *Glass Phys. Chem.* **34** 201
- Gundakaram R, Lin J G, Lee F Y, Tai M F, Shen C H, Liu R S and Huang C Y 1999 *J. Phys.: Condens. Matter* **11** 5187
- Jung W -H 2000 *J. Mater. Sci. Lett.* **19** 1307
- Jung W -H 2003 *J. Mater. Sci. Lett.* **22** 527
- Kimura T and Tokura Y 2000 *Ann. Rev. Mater. Sci.* **30** 451
- Maignan A, Martin C, Damay F, Hervien M and Raveau B 1998 *J. Magn. Magn. Mater.* **188** 185
- Maignan A, Martin C, Hervien M and Raveau B 2001 *Solid State Commun.* **117** 377
- Martin C, Maignan A, Hervien M, Antret C, Raveau B and Khomski D I 2001 *Phys. Rev.* **B63** 174404
- Meixner H and Lampe U 1996 *Sensor Actuator* **B33** 198
- Moseley P T and Williams D E 1989 *Polyhedron* **9** 1615
- Ormerod R M 2003 *Chem. Soc. Rev.* **32** 17
- Raveau R, Maignan A, Martin C, Mahendiran R and Hervien M 2000 *J. Solid State Chem.* **151** 330
- Ruddlesden S N and Popper P 1957 *Acta Crystallogr.* **10** 538
- Ruddlesden S N and Popper P 1958 *Acta Crystallogr.* **11** 54
- Sahu R K, Mohammad Q, Rao M L, Manoharan S S and Nigam A K 2002 *Appl. Phys. Lett.* **80** 88
- Skinner S J and Kilner J A 2000 *Solid State Ionics* **135** 709
- Subramanian M A, Torardi C C, Johnson D C, Pannetier J and Sleight A W 1988 *J. Solid State Chem.* **72** 24
- Sudhakar N and Rajeev K P 2004 *J. Electron. Mater.* **33** 1259
- Sudhakar N, Rajeev K P and Nigam A K 2003 *J. Appl. Phys.* **93** 8331
- Suzuki N, Noritake T, Yamamoto N and Hioki T 1991 *Mater. Res. Bull.* **26** 1
- Yankin A M, Fedorova O M, Zvereva I A, Titova S G and Balakirev V F 2006 *Glass Phys. Chem.* **32** 574
- Zhang J, Wang F, Zhang P and Yan Q 1999 *J. Appl. Phys.* **86** 1604
- Zhang J, Yan J Q, Wang F, Yuan P and Zhang P 2000 *J. Phys.: Condens. Matter* **12** 1981
- 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