STRUCTURAL, SINTERING AND ELECTRICAL PROPERTIES OF THE PEROVSKITE-TYPE
(La, Sr) (Cr, Mn) O₃

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ABSTRACT

The \( \text{LaCr}_{1-x}\text{Mn}_x\text{O}_3 \) system has been investigated to determine the best composition for high temperature electrode and fuel cell interconnector applications. Structural studies were made using a Rietveld pattern-fitting structure-refinement algorithm with X-ray powder diffraction data. The pattern fitting nature of this technique aided in the identification of phases and allowed for precise determination of the lattice parameters for the component phases. For compositions annealed at temperatures below 1200°C a single orthorhombic phase was found for \( x < 0.55 \) while a single rhombohedral phase existed for \( x > 0.60 \). A mixture of the two phases existed for intermediate compositions. Lattice parameters were shown to vary smoothly as a function of atomic substitution.

Sintering studies were done in air at temperatures below 1500°C. Significant improvement in densification was observed with substitution of 50% Mn for Cr. A density of 95% theoretical was achieved with the substitution of 70% Mn for Cr.

Electrical conductivity (d.c.) measurements were made as a function of temperature and oxygen activity. At 1000°C and 1 atm. \( \text{O}_2 \) the electrical conductivity measurements ranged from 2.2 S/cm to 20 S/cm for the compounds \( \text{LaCr}_{0.8}\text{Mn}_{0.2}\text{O}_3 \) and \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.8}\text{Mn}_{0.2}\text{O}_3 \), respectively. The conductivity showed thermal activation for all compositions. The activation energy increased as Mn was substituted for Cr in \( \text{LaCrO}_3 \) to a maximum at 20% Mn, and then decreased to its original value as the Mn content increased beyond 30%. The concentration of carriers was directly proportional to the Sr and Mn content under oxidizing conditions. A sharp decrease in the conductivity occurred for oxygen activity of less than approximately \( 10^{13} \) at 1000°C. A positive sign Seebeck coefficient was observed for all the compositions indicating p-type conductivity. The Seebeck coefficient was nearly
temperature independent and decreased linearly with substitution of Mn for Cr. Calculated carrier mobilities indicated that the substitution of Mn for Cr significantly decreased the carrier mobility. The substitution of Sr for La did not significantly increase the carrier concentration, but did increase the carrier mobility.

I. INTRODUCTION

Over the past decade, because of promising applications as electrode materials for high temperature devices, the perovskite type oxides LaMnO$_3$ and LaCrO$_3$ have received a great deal of attention. The main use of LaMnO$_3$ and LaCrO$_3$ has been as an electrode and interconnector material for MHD power generation and high temperature fuel cells, respectively. However, LaCrO$_3$ with dopants (such as Mg, Sr, Al, and Ni) is difficult to densify even at temperatures as high as 1800°C and has relatively low electrical conductivity (less than 1 S/cm at 1000°C and oxygen activity of $10^{-16}$) (1). LaMnO$_3$ doped with Sr has been used as cathode for fuel cells (2). The electrical conductivity of Sr-doped LaMnO$_3$ in an oxidizing atmosphere is very high (190 S/cm at 1000°C) (3), however, it dissociates at 1000°C and an oxygen activity of $10^{-15}$. Other perovskite structure oxides such as LaNiO$_3$ and LaCoO$_3$ have also been investigated as high temperature electrodes but, at 1000°C and in reducing conditions these oxides are also unstable to dissociation (4). The addition of Cr to those oxides has been suggested as a method of increasing the stability of those oxides towards reduction. However, the addition of Cr has two negative effects; the electrical conductivity is decreased and the ability to sinter such oxides diminishes as the Cr content increases. However, it has also been noted that stability against reducing is improved at high Cr content (La$_{0.8}$Sr$_{0.2}$Cr$_{0.6}$Ni$_{0.3}$O$_y$) (5).

In this study the substitution of Mn for Cr was investigated to see if both electrical conductivity and sinterability of LaCrO$_3$ could be improved without the deterioration of the stability under reducing condition. The purpose of this work was to develop an interconnector for solid oxide fuel cells by combining the desirable properties of LaCrO$_3$ and LaMnO$_3$, and to gain an understanding of the effect of different cation substitutions on the properties.

II. EXPERIMENTAL PROCEDURE

A number of compositions of LaCrO$_3$ - LaMnO$_3$ based powders were prepared using the liquid-mix process (6). Each composition was prepared by dissolving predetermined amounts of La carbonate, Mn carbonate, Sr carbonate, and a Cr containing solution in citric acid and ethylene glycol. The mixtures were heated on a hot plate at about 95°C until polymerization occurred. Subsequent heating at higher temperatures resulted in the decomposition of the polymer resin and allowed conversion into the desired oxide. Final calcination was done at 850°C for 8 hours. To insure that the synthesis was correct, each composition was subjected to X-ray diffraction...
analysis using a General Electric XRD-700 X-ray diffractometer scanned at a
rate 1° 2θ /min. In order to improve the X-ray diffraction patterns, a number
of the compositions were reheated to 1200°C for 4 hours. This treatment
increased both the crystallinity and the grain size of the powders (grain size
increased from 0.1 μm to 1.0 μm). X-ray diffraction patterns from these
powders were subjected to the Rietveld structural refinement procedure in order
to determine lattice parameters and phases. For the electrical conductivity and
sintering studies, some of the powders were pressed into bars with the aid of a
PVA and water binder. A compaction pressure of 1075 kg/cm² yielded 1.0 x 0.6
x 1.5 cm³ bars with a green density about 40% of theoretical. Densification was
carried out at 1475°C for 11 to 48 hours in a SiC heated box furnace. Bulk
densities were measured using xylene as a saturating liquid. Scanning electron
micrographs of the polished surface of sintered compounds were taken with a
model JEOLCO JSM -35 CF scanning electron microscope.

Electrical conductivity (d.c) and the Seebeck coefficient measurements
were measured on (0.3x0.3x1.5 cm³) rectangular shaped specimens which were
electroded with Pt paste. The specimens were then mounted between two
platinum blocks. Platinum- 10% Rh/Pt thermocouples were used to measure the
temperature at the both ends of the specimens. A Pt wire heater was wound on
the lower end of the holder in order to generate a temperature gradient along
the vertical direction. Three sets of specimens and holders were inserted into a
MoSi₂ furnace in which atmospheric control was achieved by using flowing gas
mixtures composed of either O₂ - N₂ or CO₂ - forming gas (10% H₂ - 90 N₂). A
stabilized zirconia oxygen sensor was used to monitor the oxygen partial
pressure of the gas mixture. The Seebeck coefficients were determined by
measuring temperature gradients and thermal emf’s through the common leads
of the thermocouples. Electrical conductivity measurements were made using a
two-probe, four-wire Kelvin technique in which two leads carry the current
(1mA) and the other two measure the voltage drop. The measurements were
made using a data logger, (A Hewlett Packard 3497A data acquisition/control
unit) which employs a HP-85 computer both as a control and readout device.
More details on this apparatus are available in Ref. 18.

III. RESULTS AND DISCUSSION

A. STRUCTURAL STUDIES (RIETVELD REFINEMENT)

The Rietveld technique (7,8) of pattern-fitting-structure-refinement
was used to determine precise values of the lattice parameters and assay the
phase/composition of selected specimens. This technique is based on the ability
to calculate an X-ray powder diffraction pattern when the structural parameters
for respective phases are known. Figure 1 shows the phase/composition
relationship obtained using this refinement procedure. Results showed the
existence of a single orthorhombic phase when the system has Mn content (x)
less than 0.55 moles while a single rhombohedral phase existed when the Mn
content (x) was greater than 0.60 moles. A mixture of the two phases was found
for intermediate compositions.
The parameters obtained for the orthorhombic and rhombohedral phases examined in this study exhibit a large number of overlapping and otherwise unresolved diffraction lines. For this type of overlapping the Rietveld technique has two major advantages. The first advantage is that it generates the correct number of lines to fit the observed diffraction patterns and constrains their positions based on the values of the lattice parameters for the respective phase. The second advantage in using this technique arises from the number of data points (observations) used in refining the variables of interest. Estimates of the lattice parameters are obtained using all the information available over the region of the scan; this includes overlapping lines. Using this procedure, the lattice parameters were calculated for each composition and are plotted in Figures 2 and 3 for each region. LaCrO$_2$ was found to consist of a single orthorhombic phase with lattice parameters $a = 5.5206(4) \, \text{Å}$, $b = 5.4861(4) \, \text{Å}$ and $c = 7.7742(8) \, \text{Å}$, in excellent agreement with published values (9). Lattice parameters are shown to vary smoothly as a function of Mn substitution for Cr. The lattice parameters of some compositions calculated from the Rietveld program are also listed in Table I. The end member LaMnO$_3$ had a rhombohedral structure with lattice parameters $a = 5.4724(1) \, \text{Å}$ and a rhombohedral angle 60.582° (1) in agreement with published values (10).

B. SINTERING STUDIES

The densification of the various compositions was studied as function of Mn content and time at 1475°C in air. The results are listed in Table II and illustrated in Figure 4. It was clear that substitution of Mn for Cr improved the sinterability of all compositions. At the present time there are no data to determine which mass transport mechanism is dominating the densification mechanism in the compounds. However, it is certain that Mn substitution for Cr in LaCrO$_2$ increases the sintered density. The microstructures indicated that when Sr was added as an acceptor to improve electrical conductivity, it also enhanced the sinterability. Significant improvement in densification was observed with substitution of 50% Mn for Cr, and 95% theoretical density was achieved with substitution of 70% Mn for Cr. Sintered compounds from the rhombohedral region were ground and subjected to X-ray analysis to investigate their crystal structures. It was found that they had orthorhombic structure at room temperature. This indicated a structural phase transition from rhombohedral to orthorhombic structure during the sintering. The cell volume change during this transition was from about 117Å$^3$ to 234Å$^3$ which might slightly enhance the densification through the Hedvall effect (11). However, clarification of the mechanism will have to be deferred to future studies.

C. ELECTRICAL CONDUCTIVITY STUDIES

1. TEMPERATURE DEPENDENCE

D.C. electrical conductivity measurements were made in air over the

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temperature range from 25 to 1200°C. Previous studies on \((La, Sr)CrO_3\) (12) and 
\((La, Sr)MnO_3\) (10) have shown that they have intrinsic p-type conductivity due
to the formation of cation vacancies with charge being carried by holes via the
small polaron mechanism.

For the small polaron mechanism, the electrical conductivity (13), can
be expressed as;

\[
\sigma = \frac{C}{T} \exp \left( -\frac{E}{kT} \right)
\] ........................ (1)

where C is both a charge carrier concentration and material constant, T is the
absolute temperature, E is the activation energy , and k is Boltzmann’s constant.
Therefore, for materials which obey the small polaron mechanism, a plot of log \( \sigma \) versus 1/T gives a straight line whose slope is proportional to the activation
energy.

The electrical conductivity data for \(LaCr_{1-x}Mn_xO_3\) and 
\(La_{0.9}Sr_{0.1}Cr_{1-x}Mn_xO_3\) are shown in Figures 5 and 6, respectively, as log \( \sigma \) versus reciprocal temperature. (dotted lines are taken from Ref. 14 for x = 0.0
and Ref. 10 for x = 1.0) The data were similar in both systems with an order of
magnitude drop in the conductivity when a small amount of Mn was substituted
for Cr. The electrical conductivity values lie between those of \(LaCrO_3\) and
\(LaMnO_3\) when about 40% Cr was substituted by Mn in \(LaCr_{1-x}Mn_xO_3\). Figures 7
and 8 are typical Arhennius plots of log \( \sigma \) versus reciprocal temperature.
These plots are in excellent agreement with the linear behavior predicted by
Eq.1. The activation energies for motion of charge carriers determined from
Figures 7 and 8 are plotted in Figure 9 as a function of Mn content. The
activation energy increased with Mn content to a maximum at 20% Mn
(conductivity is minimum) and then decreased to its original value as the Mn
content was increased to above 30% . The activation energies for conduction in
\(LaCr_{1-x}Mn_xO_3\) were calculated to be 0.48, 0.34, 0.27, 0.21 eV for x = 0.2, x = 0.3,
x = 0.4 and x = 0.6 ,respectively. Additional Sr content beyond 10% did not
significantly alter the activation energies.

Seebeck measurements were made to determine the type and
concentration of charge carriers. Figures 10 and 11 are the Seebeck coefficients
versus temperature for \(LaCr_{1-x}Mn_xO_3\) and \(La_{0.9}Sr_{0.1}Cr_{1-x}Mn_xO_3\). In both systems,
the substitution of Mn for Cr significantly decreased the Seebeck coefficients. A
substitution of 20% Mn for Cr in both systems changed the temperature
dependence to a nonlinear behavior. As the Mn substitution for Cr was
increased further , the Seebeck coefficients exhibited a temperature independent
behavior, indicating that the carrier mobility, rather than the carrier
concentration, was thermally activated. According to the Heikes formula this
type of behavior indicates a small polaron conduction mechanism which agrees
with the electrical conductivity measurements. Using the assumption that only
one electron is allowed on a given site and both spin and orbital degeneracy are
negligible yields an expression for the Seebeck coefficient (15);

\[
Q = \left( \frac{k}{e} \right) \left\{ \ln \left( \frac{1-x}{x} \right) + \frac{S^*}{k} \right\}
\] ........................ (2)
where \( k \) is Boltzmann's constant, \( e \) is the unit charge, \( x \) is the fraction of hopping sites which are occupied and \( S^* \) is the vibrational entropy associated with the ions surrounding a polaron on a given site. This equation leads to a temperature independent Seebeck coefficient. Usually, the entropy \( S^* \) is small enough to be negligible, therefore, the Seebeck coefficient depends only on the concentration term. Using the Seebeck data and Heikes formula, the fraction of hopping sites at 1000°C were calculated as a function of Mn content (Figure 12). As can be seen the occupied fraction of hopping sites increased as Mn content increased, indicating that conduction was taking place in the partially filled \( Mn^{3+} \) conduction band. If this was not the case, an increase in conductivity should be expected as Mn content increased. This supposition is supported from the results obtained from the activation energy variation as a function of Mn content (Figure 9). It has been shown that the activation energy for hopping polarons is inversely proportional to the separation distance between polaron sites (16). At low Mn content, the activation energy increased as a result of the large separation between Mn ions. When the Mn content increased the activation energy decreased due to the decrease in separation distance between Mn ions. The observed weak temperature dependence of the Seebeck coefficient implies that the carrier concentration is not a strong function of temperature. Therefore, the temperature dependence of electrical conductivity would be largely dependent on the mobility of charge carriers. Additional Sr substitution for La in \( LaCr_{1-x}Mn_xO_3 \) compounds did not alter either the temperature dependence or the Seebeck coefficients of these compounds. However, according to the concept of controlled valence theory, the increase of acceptor concentration in p-type materials will create increased charge carrier concentration. Seebeck coefficients measured in the high temperature region for Sr-doped compounds were found to be close to those of undoped ones. It may be concluded that additional Sr substitution for La in the Mn doped compounds does not create additional charge carriers as expected from the theory. Therefore, the electrical conductivity of these perovskite-type oxides is dominated by the mobility rather than the carrier concentration.

2. OXYGEN ACTIVITY DEPENDENCE

The d.c. electrical conductivity measurements for \( LaCr_{0.4}Mn_{0.6}O_3 \), \( La_{0.9}Sr_{0.1}Cr_{0.6}Mn_{0.4}O_3 \) and \( La_{0.9}Sr_{0.1}Cr_{0.6}Mn_{0.4}O_3 \) were made as a function of oxygen activity at 1000°C. The results are shown in Figure 13. In Figure 13, \( La_{0.9}Sr_{0.1}MnO_3 \) and \( LaCr_{0.95}Mg_{0.05}O_3 \) data are included for comparison. They are taken from Ref. 10 and Ref. 14, respectively. Seebeck measurements were also made as a function of oxygen activity at 1000°C for some compositions. It was found that the Seebeck coefficients were always positive even after the compounds decomposed. At 1000°C with decreasing oxygen activity, the Seebeck coefficients increased to a maximum then started decreasing as a result of structural decomposition. The critical oxygen activity for compounds were observed to be close to those for \( LaMnO_3 \) (About 10⁻¹⁵ atm. at 1000°C). An initial drop in the electrical conductivity of compounds was observed as oxygen activity was decreased. This must be due to the reduction in the number of
charge carriers as oxygen vacancies were introduced. This was confirmed by the oxygen activity dependence of the Seebeck coefficient at 1000°C. Figure 14 shows the experimental evidence of such a relationship between conductivity and Seebeck coefficient for \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.8}\text{Mn}_{0.2}\text{O}_{3} \). As can be seen in Figure 14, the Seebeck coefficient increased and the electrical conductivity decreased with decreasing oxygen activity. This was true until decomposition occurred.

3. MOBILITY OF CHARGE CARRIERS

The mobility of charge carriers can be determined by combining the Seebeck and electrical conductivity data. Since the Seebeck coefficients were positive, the electrical conductivity is assumed to be due to holes only. The electrical conductivity for holes is given by;

\[
\sigma = (A/\nu)pe \mu \quad \quad \quad \quad \quad \quad (3)
\]

where \( A \) is Avogadro number, \( \nu \) is the molar volume, \( p \) is the molar fraction of holes, \( e \) is the unit charge and \( \mu \) is the hole mobility. The Seebeck coefficient for holes can be represented by;

\[
Q = (k/e) \{ \ln (N\nu/\nu_0) \} \quad \quad \quad \quad \quad (4)
\]

where \( k \) is Boltzmann constant and \( N_0 \) is the density of states. Assuming that \( S^* \) is negligible, combining Eq. 3 and 4 and rearranging yields a mobility term;

\[
\mu = (\sigma / N_0 e) \exp( Qe/k) \quad \quad \quad \quad \quad (5).
\]

Using the information obtained from a structural refinement procedure (Table I), the density of states was calculated for each composition. Using these values for the density of states and the experimental data, the mobility of charge carriers for compounds were calculated from Eq. 5 as a function of temperature and Mn content. The results from these calculations are shown in Figures 15 and 16. The mobilities of charge carriers are tabulated in Table III. These results indicate that the mobility was significantly decreased by Mn substitution for Cr and increased by the substitution of Sr for La. Electrical conductivity and Seebeck results indicate that the electrical conductivity in these compounds \( \text{La}_{x}\text{Sr}_{y}(\text{Cr},\text{Mn})_z\text{O}_3 \) is dominated by the mobility of charge carriers rather than by the carrier concentration.

Note that the mobility of charge carriers for these perovskites are only approximate, since the Heikes formula which assumed that both spin and orbital degeneracy were negligible was involved in the calculation. The real situation may be more complicated than that described by Heikes formula. However, these small mobility values are consistent with the criteria given by Goodenough (17). For the small polaron mechanism, the mobility can be expressed as;

\[
\mu = (A/T) \exp(-W_H/kT) \quad \quad \quad \quad \quad (6)
\]
where $A$ is the pre-exponential factor depending on the fraction of hopping sites, $T$ is the absolute temperature, $k$ is the Boltzmann constant and $W_H$ is the activation energy for hopping. A straight line is expected in a $\ln(\mu T)$ versus reciprocal temperature plot if conduction obeys the small polaron mechanism. Figures 17 and 18 show the data for compounds plotted according to Eq. 6. Using these plots, the activation energy for carrier hopping in $(LaCr_{1-x}Mn_xO_3)$ were calculated as 0.63, 0.30 and 0.21 eV for $x=0.2$, $x=0.4$, $x=0.6$, respectively. From the Seebeck and conductivity data, it can be concluded that carrier mobility rather than the carrier concentration is thermally activated, and the activation energies for hopping obtained from the mobility data increases with Mn content, rises to maximum where the mobility is minimum, and then decreases back to its original value as Mn content increased above 30%. This behavior was similar to that observed from the electrical conductivity data. Note that within the accuracy of the measurements these activation energies for hopping are the same as those calculated from the electrical conductivity which is given in Figure 9. Data obtained from both mobility and electrical conductivity data is shown in Figure 19 for comparison.

IV. CONCLUSION

The $LaCrO_3 - LaMnO_3$ system forms a solid solution. A single orthorhombic phase was found for substitution of less than 55% Mn for Cr, a single rhombohedral phase existed for substitution of greater than 60% Mn for Cr, and a mixture of two phases for the intermediate compositions. Lattice parameters were shown to vary smoothly as a function of substitution. Mn substitution for Cr significantly improved the sinterability. Densities above 95% TD were achieved at 1475°C for the composition $La_{0.9}Sr_{0.1}Cr_3MnO_7$. The electrical conductivity and Seebeck data were interpreted by a small polaron mechanism. The carrier mobility rather than carrier concentration is thermally activated. Electronic conduction occurs in the $Mn^{3+}$ conduction band when there is as much as 20% Mn substitution for Cr. Substitution of Mn for Cr significantly decreased the carrier mobility. Additional Sr substitution for La did not result in an increase in the carrier concentration, but in the carrier mobility of the resulting ceramics.

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TABLE 1

LATTICE PARAMETERS OF COMPOSITIONS IN THE SYSTEM LaCrO₃ - LaMnO₃ CALCULATED FROM RIETVELD PROGRAM

| Composition       | a (Å)     | b (Å)     | c (Å)     | Angle ° | Structure  | Theoretical Density g/cc |
|-------------------|-----------|-----------|-----------|---------|------------|--------------------------|
| LaCrO₃            | 5.5206 (4)| 5.4861 (4)| 7.7742 (8)|         | Orthorhom. | 6.74                     |
| LaCr₁₇Mn₃₁₃       | 5.5153 (7)| 5.4808 (7)| 7.7674 (14)|         | " "       | 6.78                     |
| La₈₉Sr₁₇Cr₇Mn₃₀₃  | 5.5150 (5)| 5.4782 (5)| 7.7708 (9) |         | " "       | 6.62                     |
| LaCr₆₄Mn₄₀₃       | 5.5176 (6)| 5.4800 (7)| 7.7830 (11)|         | " "       | 6.78                     |
| LaCr₅₅Mn₅₅        | 5.5229 (2)| 5.4806 (2)| 7.7857 (3) |         | " "       | 6.79                     |
| La₈₉Sr₁₇Cr₇Mn₅₀₃  | 5.5153 (6)| 5.4700 (6)| 7.7885 (12)|         | " "       | 6.62                     |
| LaCr₄₅Mn₅₅        | 5.5235 (4)| 5.4821 (4)| 7.7867 (7) | 44 %Orth +| 6.79       |
| LaCr₄₅Mn₅₅        | 5.4655 (1)| -         | -         | 60.6850 (34) 56 %Rhom. | 6.82       |
| LaCr₄₅Mn₅₅        | 5.5251 (6)| 5.4852 (5)| 7.7770 (10)| 43 %Orth +| 6.78       |
| LaCr₄₅Mn₅₅        | 5.4633 (8)| -         | -         | 60.6840 (19) 57 %Rhom. | 6.82       |
| La₄₅Mn₆₀         | 5.4628 (4)| -         | -         | 60.6834 (8) Rhombohed. | 6.83       |
| La₈₉Sr₁₇Cr₇Mn₇₀₃  | 5.4680 (1)| -         | -         | 60.5876 (17)  " "  | 6.67       |
| LaCr₄₅Mn₅₅        | 5.4704 (1)| -         | -         | 60.6375 (20)  " "  | 6.83       |
| LaCr₄₅Mn₅₅        | 5.4679 (1)| -         | -         | 60.5821 (21)  " "  | 6.85       |
| LaMnO₃⁺            | 5.4724 (1)| -         | -         | 60.5829 (21)  " "  | 6.84       |

* Numbers in parenthesis refer to standard deviation for parameters.
  For example; a=5.5206 , S.D.=0.0004 shown as a=5.5206 (4)
### Table II

**Sintering Properties of Compounds**

| Compound          | Sinter Temp (°C) | Sinter Time (Hour) | Green Density (g/cm³) | Bulk Density (g/cm³) | % T.D. | % Porosity (open) |
|-------------------|------------------|--------------------|-----------------------|----------------------|--------|-------------------|
| LaCr$_{0.7}$Mn$_{0.3}$O$_3$ | 1475             | 11                 | 2.89                  | 4.06                 | 60     | 39                |
|                   |                  | 24                 | 2.81                  | 4.20                 | 62     | 34                |
|                   |                  | 48                 | 2.68                  | 4.35                 | 64     | 33                |
| La$_{0.9}$Sr$_{0.1}$Cr$_{0.7}$Mn$_{0.3}$O$_3$ | 1475             | 11                 | 3.17                  | 4.51                 | 68     | 35                |
|                   |                  | 24                 | 3.22                  | 4.54                 | 68.5   | 29                |
|                   |                  | 48                 | 3.11                  | 4.71                 | 71     | 26                |
| LaCr$_{0.5}$Mn$_{0.5}$O$_3$ | 1475             | 11                 | 2.73                  | 4.70                 | 69     | 29                |
|                   |                  | 24                 | 2.74                  | 5.04                 | 74     | 19                |
|                   |                  | 48                 | 3.02                  | 5.27                 | 77.7   | 13                |
| La$_{0.9}$Sr$_{0.1}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ | 1475             | 11                 | 3.15                  | 5.28                 | 80     | 18                |
|                   |                  | 24                 | 2.93                  | 5.40                 | 81.5   | 11                |
|                   |                  | 48                 | 3.14                  | 5.55                 | 84     | 10                |
| LaCr$_{0.3}$Mn$_{0.7}$O$_3$ | 1475             | 11                 | 3.19                  | 6.01                 | 88     | 1                 |
|                   |                  | 24                 | 3.16                  | 6.26                 | 92     | 1                 |
|                   |                  | 48                 | 2.99                  | 6.41                 | 94     | 1                 |
| La$_{0.9}$Sr$_{0.1}$Cr$_{0.3}$Mn$_{0.7}$O$_3$ | 1475             | 11                 | 3.19                  | 6.08                 | 91     | 1                 |
|                   |                  | 24                 | 3.10                  | 6.27                 | 94     | 1                 |
|                   |                  | 48                 | 2.98                  | 6.35                 | 95.5   | 1                 |
TABLE III

AT 1000 °C THE CALCULATED CARRIER MOBILITY FOR COMPOUNDS (La,Sr) Cr$_{1-x}$Mn$_x$O$_3$

| Compound | Mobility (0% Sr) cm$^2$/V·sec | Mobility (10% Sr) cm$^2$/V·sec |
|----------|-------------------------------|-------------------------------|
| X = 0.0  | 0.07                          | 0.12*                         |
| X = 0.2  | 0.0013                        | 0.0044                        |
| X = 0.4  | 0.0024                        | 0.0048                        |
| X = 0.6  | 0.0072                        | 0.0073                        |
| X = 1.0  | 0.045                         | 0.058**                       |

* From Ref. 15
** From Ref. 10
Figure 1. The phase/composition relationship obtained using the refinement procedure.

Figure 2. Lattice Parameters in the orthorhombic region.
Figure 3. Lattice parameter in the rhombohedral region.

Figure 4. Sintering behavior of the compounds as a function of Mn content.
Figure 5. The electrical conductivity of compounds $\text{LaCr}_{1-x}\text{Mn}_x\text{O}_3$ as a function of temperature.

Figure 6. The electrical conductivity of compounds $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3$ as a function of temperature.
Figure 7. Log (σT) vs. 1/T for compositions \((\text{LaCr}_{1-x}\text{Mn}_x\text{O}_3)\).

Figure 8. Log (σT) vs. 1/T for compositions \((\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3)\).
Figure 9. Activation energy for conductivity vs. Mn content (La,Sr)Cr$_{1-x}$Mn$_x$O$_3$ (calculated from conductivity data).

Figure 10. Seebeck coefficient of compounds as a function of temperature (LaCr$_{1-x}$Mn$_x$O$_3$).
Figure 11. Seebeck coefficient of compounds as a function of temperature ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3$).

Figure 12. Calculated fraction of hopping sites (occupied) as a function of Mn content at $1000^\circ\text{C}$ ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3$).
Log Conductivity (S/cm) vs. Log Oxygen activity for compounds at 1000°C.

Figure 13. Log Conductivity vs. Log Oxygen activity for compounds at 1000°C.

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Figure 14. Seebeck coefficient and Log conductivity as a function of oxygen activity for La$_{0.9}$Sr$_{1.1}$Cr$_{0.6}$Mn$_{0.4}$O$_3$ at 1000°C.

Figure 15. Mobility of compounds as a function of temperature (LaCr$_{1-x}$Mn$_x$O$_3$).
Figure 16. Mobility of compounds as a function of temperature 
\((\text{La}_{0.9}\text{Sr}_{1.1}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3\).)

Figure 17. \(\ln (\mu T)\) vs. reciprocal temperature for \(\text{LaCr}_{1-x}\text{Mn}_x\text{O}_3\).
Figure 18. \( \ln(\mu T) \) vs. reciprocal temperature for \( \text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3 \). (Calculated from both mobility and conductivity data).

Figure 19. Activation energy for compounds as a function of Mn content \( (\text{LaCr}_{1-x}\text{Mn}_x\text{O}_3) \). (Calculated from both mobility and conductivity data).