REVIEW OF DEFECT CHEMISTRY OF LaMnO₃ AND LaCrO₃*

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ABSTRACT

Chemical stability and cation stoichiometry determine the applicability of LaCrO₃ and LaMnO₃ as high temperature solid oxide fuel cell (SOFC) interconnects and cathodes respectively. Models for the oxidation-reduction behavior of acceptor doped LaCrO₃ and acceptor doped LaMnO₃ are reviewed. Experimental data are presented which agree with the models and show the regimes of oxygen activities and temperature over which these oxides can be expected to be stable.

1. INTRODUCTION

It is essential for the long term reliability of fuel cells that the electrodes and interconnects of fuel cells be stable, both electrically as well as structurally, at elevated temperatures in the presence of the required electrolytes and oxygen activities. A number of oxides are candidates for this application with some of the most promising being from the perovskite family. For many of the AB₃ compounds, sufficient electrical conductivity is obtainable by substitution on either the A or B sites by acceptor-or donor-type cations, depending on the intrinsic defect structure of the parent oxide. However, it is known that under certain oxygen activity conditions the electrical conductivity can decrease until the material becomes unsuitable as an electrode.

It is the purpose of this report to review the defect chemistry of the perovskite-type oxides LaMnO₃ and LaCrO₃ to show how the defect structure and electrical conductivity change as they equilibrate under various oxygen activities at elevated temperatures. Models for the oxidation-reduction behavior of both of these p-type oxides are presented.

The electrical conductivity of LaCrO₃ and LaMnO₃ is essentially due to the 3d band of the Cr ions,(1) thus an increase in conductivity can be expected as lower valence ions are substituted on either the La³⁺, Cr³⁺ or Mn³⁺ sites, resulting in the formation of Cr⁴⁺ or Mn⁴⁺. If such a substitution is compensated by the formation of oxygen vacancies, no contribution to the electronic conductivity

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is anticipated. The conditions under which equilibration of LaCrO$_3$ and LaMnO$_3$ take place will determine whether electronic or ionic compensation will be favored.

The behavior of LaCrO$_3$ and LaMnO$_3$ as shown in the relationships among its electrical conductivity, carrier concentration, oxidation-reduction kinetics, defect structure, and temperature, at various oxygen activities and dopant levels, need to be determined to fully characterize the materials. Such parameters are essential in order to construct a Kröger-Vink-type diagram showing the stability regimes.

Over the past several years we have been preparing Mg and Sr doped LaCrO$_3$ and Sr doped LaMnO$_3$ and relating the properties to proposed defect structure models. In this review, the models will be presented and the particular differences between LaCrO$_3$ and LaMnO$_3$ discussed. The principle model will be developed using Mg doped LaCrO$_3$ as an example. However, it is equally applicable to either Sr doped LaCrO$_3$ or Sr doped LaMnO$_3$.

2. PROPOSED DEFECT STRUCTURE

For simplicity, it will be assumed that p-type disorder prevails in nonstoichiometric LaCrO$_3$, all defects are fully ionized, and the large cation-to-small cation ratio is unity. Furthermore, it is assumed that the acceptor dopant, Mg$^{2+}$, substitutes for Cr$^{3+}$ on a normal lattice site. Using Kröger-Vink notation, the Schottky reaction for this compound is expressed by

$$n^+\rightleftharpoons V_{La}'''' + V_{Cr}'''' + 3V'_{O}$$  \hspace{1cm} (1)

and the equilibrium constant is

$$K_s = [V_{La}'][V_{Cr}'][V'_O]3$$  \hspace{1cm} (2)

From our assumption, the cation stoichiometry must remain constant unless a second phase has exsolved. Therefore, $[V'_{Cr}] = [V'_{La}]$ throughout the entire single-phase region. The p-type nonstoichiometric reaction is given by

$$\frac{3}{2} O_2\rightleftharpoons V_{La}'''' + V_{Cr}'''' + 3O_{O} + 6\hat{\alpha}.$$  \hspace{1cm} (3)

The equilibrium constant for this reaction is

$$K_3 = [V_{Cr}'''][p][6pO_2]$$

$$= \exp(-\Delta G_3/RT)$$  \hspace{1cm} (4)

where $\Delta G_3$ is the Gibbs free energy for Eq.3. When doped, the acceptor impurity, Mg$_{Cr}$, will possess one effective negative charge which can be compensated for either by a Cr$^{3+} \rightarrow$ Cr$^{4+}$ transition or
by the formation of oxygen vacancies. This leads to the following electrical neutrality condition

$$2[V_o^\text{''}] + p = 6[V_c^\text{''}] + [MgCr]$$

At high activity, assuming that both $[V_o^\text{''}]$ and $[V_c^\text{''}]$ are smaller than the impurity content, the neutrality condition becomes

$$p = [MgCr]$$

and from Eqs. 2 and 4

$$[V_c^\text{''}] = \frac{(K_3)^{1/2}}{[MgCr]^{3/4}} P_{O_2}^{3/4}$$

and

$$[V_o^\text{''}] = \frac{K_3^{1/3}}{K_3^{1/3}} [MgCr]^{2} P_{O_2}^{1/2}$$

respectively.

At low oxygen activities, oxygen may be lost and ionic compensation takes place through the formation of oxygen vacancies. In this case the neutrality condition becomes

$$p = [MgCr] - 2[V_o^\text{''}]$$

This condition can be expressed by

$$\text{LaCr}_1.2y\text{Cr}^{MgCryO}_3 \xrightarrow{\text{reduction}} \text{LaCr}_1.2y+2x\text{Cr}^y-x\text{MgCr}_y\text{O}_3-x + \frac{1}{2} \text{O}_2 \ (8)$$

or

$$O_o + 2\text{Cr}^c \xrightarrow{\text{oxidation}} 2\text{Cr}^c + V_o^\text{''} + \frac{1}{2} \text{O}_2 \ (9)$$

where y is the amount of dopant and x is the concentration of oxygen vacancies.

The equilibrium constant for reaction 9 can be expressed as either

$$K_9 = \frac{[CrCry]^2[V_o^\text{''}]}{[CrCry]^2 P_{O_2}^{1/2}}$$

or

$$K_9 = \frac{(1-2y+2x)^2 x}{(y-2x)^2} P_{O_2}^{1/2}$$

The mass action equation then becomes

$$K_9 = \exp\left[-(\Delta G_s - \Delta G_3)/3RT\right]$$
where $\Delta G_g$ = free energy of formation for Schottky defects, $\Delta G_3$ is free energy of formation for cation vacancies, and $(\Delta G_g - \Delta G_3)/3$ is the free energy of formation for one mole of $V'_o$ in acceptor-doped LaCrO$_3$.

Equation 10 can be solved to yield

$$2x - y - \frac{\sqrt{4Kg}}{2}[(8yKgP_0^2 + 1)^{1/2} - 1].$$ (11)

The electrical conductivity $\sigma$ is given by

$$\sigma = e\mu p$$

where $e$ is the electron charge, $\mu$ the mobility, and $p$ the concentration of carriers which, from the model, is equal to $y - 2x$. Thus Eq.11 can be rearranged to give

$$\sigma = \frac{e}{4Kg}P_0^{1/2}[(8yKgP_0^2 + 1)^{1/2} - 1].$$ (12)

At the high-$P_0$ limit, Eq.11 reduces to $x = 0$ and Eq.12 reduces to $\sigma = e\mu y$, whereas in the low-$P_0$ regime the respective equations are reduced to:

$$p = \frac{y-2x}{y} = \frac{P_0^{1/4}}{(2yKg)^{1/2}}$$ (13)

or

$$\sigma = e\mu \frac{y^{1/2}}{2Kg} P_0^{1/4}$$ (14)

and

$$\sigma/\sigma_R = \frac{P_0^{1/4}}{(2K_{11}y)^{1/2}},$$ (15)

where $\sigma_R$ is the conductivity when acceptors are compensated electronically.

In this $P_0$ limit, the acceptors become compensated by oxygen vacancies and $[NgCr] = 2[V'_o]$. Thus, it is anticipated that $\sigma$ will decrease with decreasing $P_0$ as $P_0^{1/4}$ as the electrical compensation changes from electronic to ionic.

Thermogravimetric and electrical-conductivity measurements as a function of $P_0$ and temperature are used to evaluate the equilibrium constants. Diagrams showing the predominant defects under various thermal and oxygen activity conditions can then be constructed. This allows the behavior of the electrical conductivity to be predicted under variable oxidizing and reducing conditions.

The model developed for LaCrO$_3$ describes the electrical conductivity of LaMnO$_3$ quite well. However, LaMnO$_3$, even when Sr doped, has excess oxygen at high oxygen activity and in the lowest
oxygen activity Mn$^{2+}$ tends to form and the structure dissociates into its binary components. Thus to explain the defect concentrations the influence of cation vacancies and Mn$^{2+}$ must be considered.\(^{(3)}\)

In the oxygen excess region the reduction of La$_{1-y}$Sr$_y$MnO$_{3+x}$ may be expressed as

$$\text{La}_{1-y}\text{Sr}_y\text{V}^{Mn}_x\text{La}_x\text{Mn}_{1-y-2x}\text{Mn}_y\text{V}^{Mn}_x\text{O}_{3+x}$$

$$\leftrightarrow \text{La}_{1-y}\text{Sr}_y\text{Mn}_{1-y}\text{Mn}_y\text{O}_3 + \frac{x}{2} \text{O}_2$$  \hspace{1cm} (16)

where y represents the dopant and x the excess oxygen concentration. In terms of reactants this reaction can be simplified to be

$$V^{La}_x + V^{Mn}_x + 6\text{Mn}_Mn + 3\text{O}_2 \leftrightarrow 6\text{Mn}_Mn + \frac{3}{2} \text{O}_2$$  \hspace{1cm} (17)

If it is further assumed that $[V^{La}_x] = [V^{Mn}_x]$, then the equilibrium constant for this reaction is given by

$$K_{17} = [\text{Mn}_Mn]^6 \text{P}_{O_2}^{3/2} / ([V^{Mn}_x]^2 [\text{Mn}_Mn]^6 [O_2]^3)$$  \hspace{1cm} (18)

which in terms of mole fraction becomes

$$K_{17} = (1-y-2x)^6 \text{P}_{O_2}^{3/2} / ((x/3)^2 (y+2x)^6 (3+x)^3)$$  \hspace{1cm} (19)

For a given dopant level y, $K_{17}$ can be found from the weight loss vs. $\text{P}_{O_2}$ experimental data by using Eq.19. Theoretical curves in the high $\text{P}_{O_2}$ region were generated by using $K_{17}$ and the proposed metal vacancy model.

As further reduction occurs the Sr dopants are compensated by holes and Eq.9 prevails and the equilibrium constant is given by Eq.10. Since at very low $\text{P}_{O_2}$ part of the Mn ions are expected to be divalent, the general neutrality condition can be represented by

$$[\text{Sr}^{La}] + [\text{Mn}^{Mn}] = 2[V^{O}_x] + [\text{Mn}^{Mn}].$$  \hspace{1cm} (20)

The relation between $[\text{Mn}^{Mn}]$ and $[\text{Mn}^{Mn}]$ is given by

$$2\text{Mn}^{Mn}_Mn \leftrightarrow \text{Mn}^{Mn}_Mn + \text{Mn}^{Mn}_Mn$$  \hspace{1cm} (21)

with

$$K_{21} = [\text{Mn}^{Mn}_Mn] [\text{Mn}^{Mn}_Mn] / [\text{Mn}^{Mn}_Mn]^2.$$  \hspace{1cm} (22)

In order to maintain the fixed A/B ratio, the following equation has to be maintained

$$x [\text{Mn}^{Mn}_Mn] + [\text{Mn}^{Mn}_Mn] + [\text{Mn}^{Mn}_Mn] = 1.$$  \hspace{1cm} (23)
By combining the experimental TG data with the equation 19 the equilibrium constants can be calculated and the theoretical isotherms for the $P_{O_2}$ range investigated generated.

3. EXPERIMENTAL PROCEDURE

The undoped and Sr-doped LaMnO$_3$ and Mg and Sr doped LaCrO$_3$ specimens were prepared by a liquid mix method similar to that first described by Pechini.(6) In all cases, the A/B ratio (ABO$_3$) was maintained as unity. The starting chemicals were reagent grade La carbonate, Mn carbonate, Sr carbonate, Cr nitrate and Mg carbonate. The desired compositions were prepared by dissolving quantitative amounts of selected carbonates into solutions of citric acid, ethylene glycol and water.(7) Upon removal of the excess solvent by heating, transparent solid resins containing the metals in solid solution were formed. Calcination of the resin intermediates at 800°C for 8 hours removed the organic constituents, leaving the desired ceramic compositions in a fine, uniform and chemically combined state. For all compositions, X-ray diffraction analysis showed only the perovskite structure. No second phase was detected, implying that the desired solid solution was achieved.

Thermogravimetric measurements were made in a TG system designed to measure weight changes on a powder sample, 70-80 g, to an accuracy of ±1 mg (±6 X 10$^{-5}$ mole oxygen). Measurements were conducted at 1000 to 1400°C at an oxygen activity of 10$^{-17}$ to 1 atm, with the oxygen activity being monitored by a calibrated zirconia sensor. Details of the apparatus are given elsewhere.(4).

Electrical conductivity measurements were conducted on dense and porous rectangular bars with four embedded Pt wires welded to Pt leads and attached to a four-terminal digital voltmeter. Conductivity measurements were carried out at 1000 - 1400°C in an oxygen activity of 10$^{-17}$ to 1 atm.

In another apparatus, the Seebeck coefficient and dc electrical conductivity were sequentially measured on the same specimen. The specimen was situated between two Pt blocks. Two Pt - (Pt-10%Rh) thermocouples were used to monitor the temperatures at the ends of the specimen. A Pt wire heater was wound on the lower end of the holder to generate a temperature gradient along the longitudinal direction.

4. RESULTS AND DISCUSSION

A. LaCrO$_3$

Typical TG results for LaCrO$_3$ are displayed in Figs. 1 and 2, which show the experimental data plotted in terms of oxygen deficiency as a function of temperature and oxygen activity for a
constant dopant concentration, and as a function of dopant content and oxygen activity at a constant temperature, respectively. Figure 1 shows that the oxygen activity at which maximum nonstoichiometry occurs shifts to lower values as the temperature is decreased from 1366 to 1014°C, whereas Fig. 2 shows that the degree of nonstoichiometry increases as the amount of dopant increases at any given oxygen activity. The solid lines are those predicted from the model and represent the best fit solution of the equilibrium constant expression.

The temperature dependence of the equilibrium constant, $K_9$ for reaction (9) was determined. It was found that for up to 10 at% Mg the enthalpy of the reaction appears to be independent of Mg constant; however, at higher Mg content this is not true. For example, up to 10 at% Mg, this value was found to be $272 \pm 16$ kJ/mol ($2.8 \pm 0.2$ ev), whereas it increased to $331 \pm 12$ kJ/mol ($3.4 \pm 0.1$ ev) for 20 at% Mg. X-ray diffraction data (7) indicate that the 20-at% Mg sample is a two-phase system and that under oxidizing conditions the phase boundary is at about 15 at% Mg. Accordingly, an expression for the equilibrium constant of the reaction within the single phase region (up to 10 at% Mg) was found to be:

$$K_9 = (2.1 \times 10^4) \exp(-\Delta H/RT) \quad (24)$$

where $\Delta H = 272 \pm 16$ kJ/mol ($2.8 \pm 0.2$ ev) and represents the enthalpy of formation of oxygen vacancies in Mg-doped LaCrO$_3$.

Figure 3 displays typical conductivity results plotted as log conductivity versus log $P_O_2$ and compared to a calculated plot, using the equilibrium constants determined by the TG data. While there is considerable scatter present and the truncation of the reaction restricts the ionically compensated region, there still is good correlation with the model throughout the entire composition range except for the 20% Mg sample where the dopant concentration appears to exceed the solubility limit (7) and notable deviation from the model was observed. The activation energy for the mobility was determined from Arrhenius plots of $\ln (\sigma T)$ vs. $1/T$ and found to be $22.3 \pm 7$ KJoul/mole ($0.23 \pm 0.07$ ev) which is in reasonable agreement with Karim and Aldred’s (6) data. However, our mobility values appear to be about an order of magnitude lower than those for the Sr doped samples implying that Mg which substitutes for Cr on the "B" sites is significantly different than Sr substituting La on the "A" sites.

A plot of conductivity vs. carrier concentration ($y-2x$) is shown in Figure 4 which confirms the assumption that the $V_0$ directly compensate the Mg ions and that the mobility does not change under the experimental conditions. Our data show a slight depression at about 80-90% of the maximum expected carrier concentration, this might be due to a band component that exists in doped but uncompensated LaCrO$_3$ and scattering or trapping by $V_0$. Otherwise, the results show a linear dependence of carrier concentration on conductivity for $y-2x$ values less than 0.05 regardless of the dopant
level, implying that the mobility is constant and approximately equal \( 5 \times 10^{-6} \text{m}^2/\text{V}\cdot\text{sec} \) which is about a factor of 5 lower than that reported by Karim and Aldred\(^{(8)}\) (2.5 \times 10^{-5} \text{m}^2/\text{V}\cdot\text{sec} for 2\% \text{Sr}). This tends to agree with the higher conductivities that they observed.

B. \text{LaMnO}_3

For \text{Sr}-doped \text{LaMnO}_3, the oxidized samples exhibited single phase X-ray patterns while the reduced samples were multiphase. The X-ray diffraction analysis showed that under the most reducing conditions (1200°C, 10^{-16} \text{atm}) \text{Sr}-doped \text{LaMnO}_3 completely dissociated into \text{La}_2\text{O}_3, \text{MnO}, \text{SrMnO}_3 and \text{La}_2\text{MnO}_4. Upon reoxidation, the reduced samples regained their original single phase X-ray patterns indicating that the redox cycle is reversible. The TG results for \text{La}_{1-y}\text{Sr}_y\text{MnO}_3 (y=0.01, 0.1 and 0.2) are shown in figures 5 and 6 in which the symbols represent the experimental data while the lines were calculated. As can be seen in figures 5 and 6 the calculated isotherms fit the data quite well.

The electrical conductivity was measured from room temperature to 1200°C as function of \( P_{O_2} \) and \text{Sr} content. The results are shown in figures 7 and 8. Typical results for the effects of \text{Sr} content on conductivity are presented in figure 8.

Both undoped and \text{Sr}-doped \text{LaMnO}_3 showed common characteristics:

- Little \( P_{O_2} \) dependence was observed in a range of high \( P_{O_2} \) and this range narrows with increasing temperature.

- As reduction proceeded, the electrical conductivity decreased as \( P_{O_2} \) which agrees well with Eq.14.

- An abrupt decrease of the electrical conductivity occurred under very reducing conditions. These data were too low to be included in figures 7 and 8. However, by comparing with the previous TG data, it was found that the abrupt decrease in electrical conductivity was due to the decomposition of the perovskite phase. For each isotherm shown in figures 7 and 8, the symbol at the lowest \( P_{O_2} \) value indicates the "critical" point, i.e., the lowest \( P_{O_2} \) before the oxide dissociated into multiple phases. Upon reoxidation, very good reversibility was found.

- The critical \( P_{O_2} \) shifted to higher \( P_{O_2} \) when the temperature and/or the dopant concentration was increased.

When the temperature was below 1000°C, the electric conductivity increased rapidly with increasing temperature. For temperature above 1000°C, the temperature dependence of electric conductivity shows a transition from positive to negative temperature dependence as the \text{Sr} content increased to 20\% suggesting a semiconducting to metallic transition. According to the previous studies for \text{LaCoO}_3,\(^{(9)}\) such a
semiconducting-metallic transition may be due to a localized to collective electron transition. Similar results were also found for other La-site substituted lanthanum manganites of the type La$_{1-x}$M$_x$MnO$_3$ (M=Pb$^{2+}$, Ba$^{2+}$, Ca$^{2+}$).\(^{(10,11)}\)

At temperature below 1000°C, the activation energies were determined using the expression derived for the small polaron mechanism,

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

where A is the pre-exponential factor, k is Boltzmann's constant, T is the absolute temperature and E is the activation energy. With the application of Eq.9, the hopping energy for undoped LaMnO$_3$ under oxidizing conditions was calculated to be 0.19±0.01 eV which is lower than the 0.25 eV reported by Goodenough.\(^{(12)}\) Since LaMnO$_3$ possesses different Mn$^{4+}$ content depending upon the preparation conditions, this small difference in activation energy is understandable. Hopping energies were calculated as 0.19±0.01, 0.16±0.01, and 0.09±0.01 eV for 5, 10 and 20 Mol % Sr doped LaMnO$_3$, respectively.

The Seebeck coefficients for undoped LaMnO$_3$, and 5, 10 and 20 Mol % Sr-doped LaMnO$_3$ were measured as a function of temperature with the results shown in figure 9. The positive Seebeck coefficients indicate that these oxides are p-type. The variation of Q for these (La,Sr)MnO$_3$ samples in the temperature range investigated is relatively small when compared with that observed for other kinds of La perovskites such as LaCrO$_3$ and (La,Sr)FeO$_3$.\(^{(13,14)}\) According to Eq.10, the weak temperature dependence of Q implies that the carrier concentration is nearly temperature independent. Therefore, the temperature dependence of electrical conductivity would depend largely on the mobility.

Seebeck measurements were made as a function of $P_{O_2}$ and temperature. Typical results for Sr-doped LaMnO$_3$ are shown in figure 10. With decreasing $P_{O_2}$, the Seebeck coefficient increased to a maximum after which it became negative. These negative values are not included in figure 10. The $P_{O_2}$ at which the Seebeck coefficient changed from positive to negative was the same as the "critical $P_{O_2}$" observed in TG and electrical conductivity data.

Even though the absolute values of the measured Seebeck coefficients in the (La,Sr)MnO$_3$ system are smaller than the 100 $\mu$V/$^\circ$K criterion suggested by Goodenough,\(^{(15)}\) for the following we assume the small polaron hopping mechanism derived by Heikes.\(^{(16)}\)

This relationship is

\[
Q = \pm \frac{k}{e} \ln \left(\frac{1-x}{x} + \frac{S^*}{k}\right)
\]
where the plus and minus signs indicate p-type and n-type carriers, respectively, \( K \) is Boltzmann's constant, \( x \) is the fraction of hopping sites which are occupied, and \( S^* \) is the vibrational entropy. When \( S^* \) is assumed small enough to be negligible, the Seebeck coefficient depends only on the concentration term. This equation leads to a temperature-independent Seebeck coefficient. By using Eq.26 and assuming that the entropy \( S^* \) is negligible, the fraction of sites occupied at 1000°C in an oxygen atmosphere was calculated to be 0.39 and 0.41 for undoped and 20 Mol% SrO-doped LaMnO\(_3\), respectively. These calculated fractions of hopping sites are clearly too high to result from doping alone. Similar behavior has been reported in the La\(_{1-y}\)Sr\(_y\)CoO\(_3\)-\(x\) system.(17) This may indicate that the conduction mechanism is more complicated than that proposed by Heikes in that another source of carriers may be involved in the transport mechanism. For example, carriers originating from the band to band transition may be contributing to the conduction at elevated temperatures. Analogous to the (La,Sr)CoO\(_3\) system, at elevated temperatures (La,Sr)MnO\(_3\) may have a position between a metal and semiconductor. Furthermore, since the calculated carrier concentrations for La\(_{8}\)Sr\(_2\)MnO\(_3\) and undoped LaMnO\(_3\) are nearly the same, it may be concluded that the electrical conductivity for these LaMnO\(_3\) based perovskites is dominated by the mobility rather than by the carrier concentration.

The mobility was determined by combining the Seebeck and electrical conductivity data. Figures 11 and 12 show the results as a function of temperature, \( P_{O_2} \) and Sr content. At 1000°C the maximum mobility for undoped LaMnO\(_3\) and La\(_{8}\)Sr\(_2\)MnO\(_3\) was calculated to be 0.045 and 0.071 cm\(^2\)/Vs, respectively. These results showed that the mobility of undoped LaMnO\(_3\) was appreciably increased by the addition of Sr. From the previous sections, the electrical conductivity of undoped LaMnO\(_3\) was found to be enhanced by the addition of Sr without appreciably altering the carrier concentration. It is concluded that the electrical conductivity for these LaMnO\(_3\) based perovskites is dominated by the mobility rather than by the carrier concentration.

Note that the values of mobility for LaMnO\(_3\) based perovskites calculated above are only approximate, since the Heikes formula which assumed that both spin and orbital degeneracy were negligible was used in the calculation.(16) 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.(15)

5. Conclusions

1. Both LaCrO\(_3\) and LaMnO\(_3\) are p-type conductors.

2. Both the TG and electrical conductivity data support the models for the oxidation-reduction behavior of both oxides.
3. At 1000°C LaCrO$_3$ is stable towards reduction, but LaMnO$_3$ dissociates for $P_{O_2} \leq 10^{-14}$ atm.

4. LaCrO$_3$ obeys the small polaron hopping mechanism of conductivity from room temperature to 1400°C on oxygen atmospheres as low as $10^{-18}$ atm.

5. LaMnO$_3$ obeys the small polaron mechanism only to about 1000°C after which metallic type behavior is observed.

6. The mobilities for each oxide ranged from 0.05 to 0.1 cm$^2$/v.sec at 1000°C.

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Figure 1. Moles oxygen weight loss per mole sample as a function of log $P_{O_2}$ at various temperatures for 5 at% Mg-doped LaCrO$_3$.

Figure 2. Moles oxygen weight loss per mole sample as a function of log $P_{O_2}$ and dopant content at 1255°C.
Figure 3. Plots of log conductivity vs. log $P_{O_2}$ at 1200°, 1250° and 1300°C for 2 at% Mg-doped LaCrO$_3$.

Figure 4. Plots of conductivity vs. (y-2x) for various levels of Mg-doped LaCrO$_3$.
Figure 5. Moles oxygen weight loss per mole sample vs. Log $P_{O_2}$ for various Sr-dopant levels. The solid lines are calculated from model and the linearized equilibrium constants.

Figure 6. Moles oxygen weight loss per mole sample as a function of Log $P_{O_2}$ at various temperatures.
Figure 7. Log conductivity vs. Log $P_{O_2}$ for La$_{0.8}$Sr$_{0.2}$MnO$_3$ at various temperatures. The solid lines are calculated from the model.

Figure 8. Log conductivity vs. Log $P_{O_2}$ for various Sr-dopant levels at 1000°C.
Figure 9. Seebeck coefficient vs. temperature for various Sr-dopant levels.

Figure 10. Seebeck coefficient vs. Log $P_{O_2}$ for La$_{0.8}$Sr$_{0.2}$MnO$_3$ at various temperatures.
Figure 11. Mobility vs. temperature for LaMnO$_3$, Sr-doped LaMnO$_3$. The measurements were done in O$_2$.

Figure 12. Mobility vs. Log $P_{O_2}$ for La$_{0.8}$Sr$_{2}$MnO$_3$ at various temperatures.