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Defect Structure of Mg-Doped LaCrO₃ Model and Thermogravimetric Measurements

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Chemical stability and cation stoichiometry determine the applicability of LaCrO₃ as a high-temperature oxide electrode. A model for the behavior of acceptor-doped LaCrO₃ as a function of oxygen activity is proposed. The model is in agreement with experimental data on Mg-doped LaCrO₃. Stability regimes and compensation mechanisms at various oxygen activities and temperature are presented.

I. Introduction

MATERIALS with high electrical conductivity which can be used in corrosive environments as well as at elevated temperatures have been in great demand over the past several years. As a result of their high melting points and high electronic conductivity, rare earth chromites have been quite attractive for such an application. One of the promising candidate materials is LaCrO₃, which satisfies many of the high-temperature electrode requirements for magnetohydrodynamic (MHD) power generators and fuel cells. However, volatilization and possibly corrosion impose certain limitations on the use of LaCrO₃. Several investigations¹⁻³ have been reported relating the role of chemical composition and cation stoichiometry to volatilization and electrical conductivity of LaCrO₃. These studies showed that materials such as LaCrO₃ and MgCr₂O₄ meet many of the requirements, except volatilization and chemical stability at the operating temperatures. For such applications, the required stability of properties over a wide oxygen-activity range at temperatures to 1700°C, as well as the necessity of fabrication into nonporous structures, demand a thorough understanding of the behavior of these materials. For example, due to grain growth, densification of high Cr-content compounds, such as LaCrO₃, is very difficult under ambient atmospheric conditions. However, control of the oxygen activity near that specified by the Cr/Cr₂O₃ phase boundary suppresses grain growth and allows maximum densification to occur.⁴⁻⁷ In another study it was found that the volatilization of LaCrO₃ at temperatures above 1600°C could be substantially reduced by the substitution of about 10% of Cr by Al with little degradation of other properties such as electrical conductivity.^{3,7}

The electrical conductivity in LaCrO₃ is essentially due to the 3d band of the Cr ions.⁸ Thus, electronic conductivity can be enhanced by substituting a lower-valence ion on either the La or Cr sites, with the formation of Cr⁴⁺. However, if such substitution is compensated by the formation of oxygen vacancies no additional contribution to the electronic conductivity will be anticipated. Whether such a substitution will favor either electronic or ionic compensation will depend on the conditions under which equilibration of LaCrO₃ takes place. Even though densification requires a reducing atmosphere, the conductivity can be appreciably increased by subsequent equilibration in an oxidizing atmosphere. Meadowcroft¹ observed a three-orders-of-magnitude increase in conductivity of La_{1-x}Sr_xCrO₃ after equilibration in an oxidizing atmosphere. However, equilibration in a reducing atmosphere caused an appreciable increase in the resistivity. Faber *et al.*⁹ suggested that La_{0.84}Sr_{0.16}CrO₃ is a *p*-type conductor and its conductivity arises from the presence of multivalent Cr ions due to Sr doping. Anderson *et al.*¹⁰ reported that substitution of an iso-

valent ion, e.g., Al³⁺ in LaCrO₃, increases the thermal expansion coefficient, decreases the electrical conductivity, and suppresses the orthorhombic-rhombohedral transformation, whereas aliovalent substitutions, e.g., Mg²⁺, cause an appreciable increase in the electrical conductivity. Earlier studies¹¹ on undoped LaCrO₃ indicate that it is a *p*-type oxide and becomes nonstoichiometric through the formation of cation vacancies.

For a better understanding of the behavior of LaCrO₃, the relationship between its electrical conductivity, oxidation-reduction kinetics, defect structure, and temperature, at various oxygen activities and dopant levels, need to be determined. Such parameters are essential in order to construct a Kröger-Vink-type diagram showing the stability regimes of LaCrO₃. In this study several Mg-doped LaCrO₃ compounds were prepared and their properties determined and related to the proposed defect structure model.

II. Proposed Defect Structure

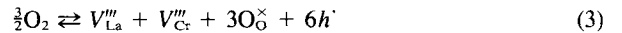
For simplicity, it will be assumed that *p*-type disorder prevails in nonstoichiometric LaCrO₃, all defects are fully ionized, and the large cation-to-small cation ratio is unity. Furthermore, it is assumed that the acceptor dopant, Mg²⁺, substitutes for Cr³⁺ on a normal lattice site. Using Kröger-Vink notation,¹² the Schottky reaction for this compound is expressed by



and the equilibrium constant is

$$K_s = [V_{La}'''] [V_{Cr}'''] [V_O^{\bullet\bullet}]^3 \quad (2)$$

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



The equilibrium constant for this reaction is

$$K_3 = [V_{Cr}''']^2 [p]^6 P_{O_2}^{-3/2} = \exp(-\Delta G_3/RT) \quad (4)$$

where ΔG_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 Cr³⁺ → Cr⁴⁺ transition or by the formation of oxygen vacancies. This leads to the following electrical neutrality condition

$$2[V_O^{\bullet\bullet}] + p = 6[V_{Cr}'''] + [Mg_{Cr}'] \quad (5)$$

At high oxygen activity, assuming that both $[V_O^{\bullet\bullet}]$ and $[V_{Cr}''']$ are smaller than the impurity content, the neutrality condition becomes

$$p = [Mg_{Cr}']$$

and from Eqs. (4) and (2)

$$[V_{Cr}'''] = \frac{(K_3)^{1/2}}{[Mg_{Cr}']^3} P_{O_2}^{3/4} \quad (6)$$

and

$$[V_O^{\bullet\bullet}] = \left(\frac{K_s}{K_3}\right)^{1/3} [Mg_{Cr}']^2 P_{O_2}^{-1/2} \quad (7)$$

respectively.

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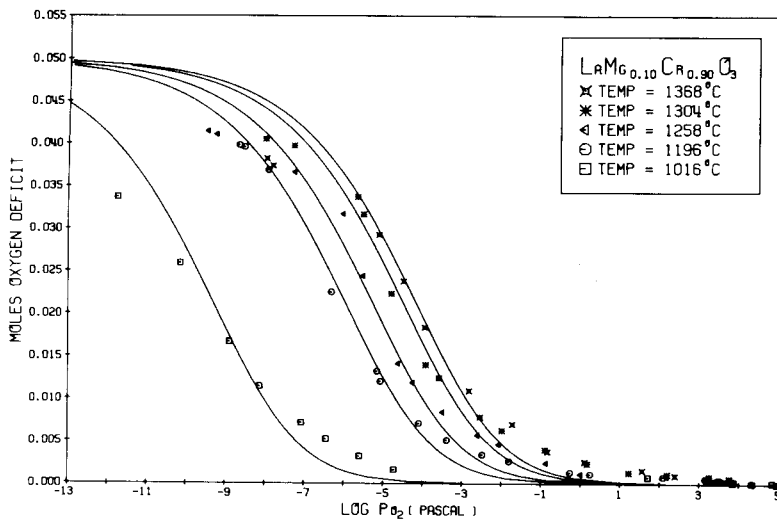


Fig. 1. Thermogravimetric measurements of oxygen deficit as a function of P_{O_2} and temperature for $LaCrO_3$ doped with 10 mol% MgO .

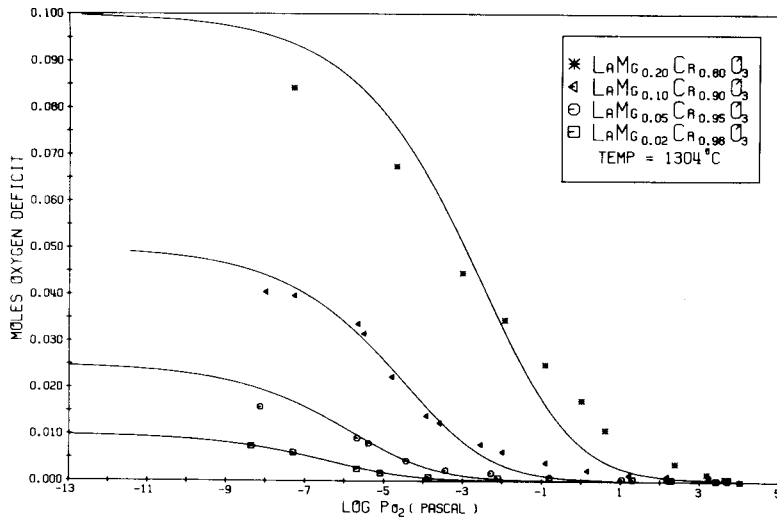
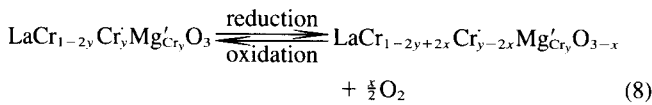


Fig. 2. Effect of dopant on oxygen deficit at varied P_{O_2} s and $1304^\circ C$.

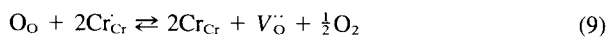
At low oxygen activities, oxygen may be lost and ionic compensation may take place through the formation of oxygen vacancies. In this case the neutrality condition becomes

$$p = [Mg'_{Cr}] - 2[V\ddot{O}]$$

This condition can be expressed by



or



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

$$K_9 = \frac{[Cr_{Cr}]^2[V\ddot{O}]}{[Cr_{Cr}]^2} P_{O_2}^{1/2}$$

or

$$K_9 = \frac{(1 - 2y + 2x)^2 x}{(y - 2x)^2} P_{O_2}^{1/2} \quad (10)$$

The mass action then becomes

$$K_9 = \exp[-(\Delta G_s - \Delta G_3)/3RT]$$

where ΔG_s = free energy for formation of Schottky defects, ΔG_3 is free energy for formation of cation vacancies, and $(\Delta G_s - \Delta G_3)/3$ is free energy for formation of one mole of $V\ddot{O}$ in acceptor-doped $LaCrO_3$.

Equation (10) can be solved to yield

$$2x = y - \frac{P_{O_2}^{1/2}}{4K_9} [(8yK_9 P_{O_2}^{-1/2} + 1)^{1/2} - 1] \quad (11)$$

Now the electrical conductivity σ is given by

$$\sigma = e\mu p$$

where e is the electron charge, μ 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

$$\sigma = \frac{e\mu}{4K_9} P_{\text{O}_2}^{1/2} [(8yK_9 P_{\text{O}_2}^{-1/2} + 1)^{1/2} - 1] \quad (12)$$

At the high- P_{O_2} limit, Eq. (11) reduces to $x = 0$ and Eq. (12) reduces to $\sigma = e\mu y$, whereas in the low- P_{O_2} regime the respective equations are reduced to:

$$\frac{y - 2x}{y} = \frac{P_{\text{O}_2}^{1/4}}{(2yK_9)^{1/2}} \quad (13)$$

and

$$\sigma = e\mu \left(\frac{y}{2K_9} \right)^{1/2} P_{\text{O}_2}^{1/4} \quad (14)$$

In this P_{O_2} limit, the acceptors become compensated by oxygen vacancies and $[\text{Mg}'_{\text{Cr}}] = 2[V_{\text{O}}]$. Thus, it is anticipated that σ will decrease with decreasing P_{O_2} as $P_{\text{O}_2}^{1/4}$, as the electrical compensation changes from electronic to ionic.

Thermogravimetric and electrical-conductivity measurements as a function of P_{O_2} and temperature are used to evaluate the equilibrium constants so that diagrams showing the predominant defects under various thermal and oxygen activity conditions can be constructed. This allows the behavior of the electrical conductivity of LaCrO_3 to be predicted under variable oxidizing and reducing conditions. In this paper, analysis of the thermogravimetric data and their correlation to the model is presented. Electrical conductivity results and resulting stability diagrams are the subjects of a later publication.

III. Experimental Procedure

A series of Mg-doped LaCrO_3 compositions were prepared by the liquid-mix process.¹³ The La/(Mg + Cr) ratio was maintained at unity as the Mg content varied from 0 to 20 mol%. Weight-change experiments were conducted using a thermogravimetric apparatus which is designed to measure weight changes on 50- to 80-g samples to an accuracy of ± 1 mg ($\approx 10^{-5}$ moles) in oxygen activities ranging from 10^{-12} to 10^5 Pa and at temperatures up to 1450°C . The furnace temperature was controlled to $\pm 1^\circ\text{C}$. Details of the TG apparatus have been given elsewhere.¹⁴ The oxygen activity was maintained by flowing gas mixtures of either N_2/O_2 or $\text{CO}_2/\text{H}_2/\text{N}_2$, which were monitored by a calibrated ZrO_2 oxygen sensor.

IV. Results and Discussion

The amount of oxygen deficiency for samples equilibrated as a function of oxygen-activity temperature and acceptor dopant was determined by TG measurements. As an example of these measurements, data for $\text{LaMg}_{0.10}\text{Cr}_{0.90}\text{O}_3$ equilibrated at $T = 1016^\circ$ to 1368°C are presented in Fig. 1. The solid lines are computed from the equilibrium constant expression, Eq. (11), using the best fit of the experimental data. The results indicate a good agreement between the experimental data and the proposed defect-structure model. Furthermore, the figure shows that the oxygen activity at which maximum nonstoichiometry occurs shifts to lower values as the temperature is decreased from 1368° to 1016°C .

The dependence of oxygen deficiency on dopant concentration and P_{O_2} is illustrated in Fig. 2 for data obtained at 1300°C . This figure shows that the degree of nonstoichiometry increases as the amount of dopant increases at any given oxygen activity. As a verification of the model, the concentration of oxygen vacancies at any given oxygen activity, within the region where oxygen-vacancy compensation is expected to prevail, was found to be a linear function of $[\text{Mg}]^2$, as predicted by Eq. (7).

The carrier concentration for samples doped with increasing Mg content at 1300°C was calculated from TG data and plotted in Fig. 3 as a function of P_{O_2} . In agreement with Eq. (13), the relative carrier concentration appears to have a one-fourth power dependence on the oxygen activity in the region where oxygen compensation is expected (10^{-10} to 10^{-5} Pa). The figure also indicates that the transition from ionic to electronic compensation occurs at relatively higher P_{O_2} as the Mg content increases, as expected from

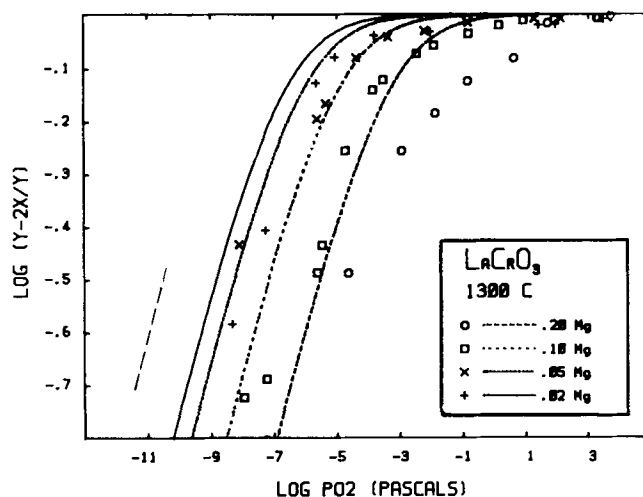


Fig. 3. Relative carrier concentration as a function of P_{O_2} and Mg content at 1300°C (measured by TG).

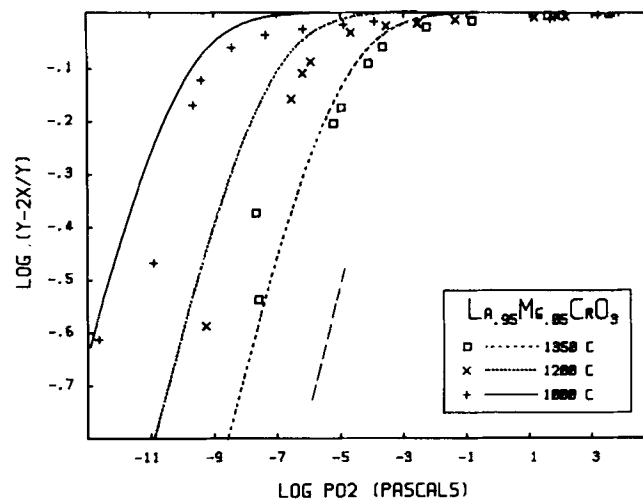


Fig. 4. Relative carrier concentration as a function of P_{O_2} and temperature for LaCrO_3 doped with 5 mol% Mg (measured by TG).

the model. The effect of temperature on the carrier concentration is shown in Fig. 4, in which the carrier concentration is plotted as a function of P_{O_2} for a constant (5 mol% Mg) dopant concentration. In the ionic compensation region, the carrier concentration appears to be in agreement with the oxygen-activity dependence proposed by the model within the temperature range investigated (1000° to 1350°C). As expected, the figure further indicates that, in the intermediate P_{O_2} range, where electronic compensation predominates, the carrier concentration is independent of both temperature and P_{O_2} . The transition from P_{O_2} dependence to independence shifts to higher oxygen activities as the temperature of equilibration increases from 1000° to 1350°C . A plot of log carrier concentration as a function of $P_{\text{O}_2}^{1/4}$ is expected to be linear in the region where ionic compensation is predominant. This is illustrated in Fig. 5 for 5 mol%-doped LaCrO_3 equilibrated at $T = 1000^\circ$ to 1400°C .

The equilibrium constant K_9 was calculated from TG data as a function of temperature and dopant concentration. The values obtained for samples doped with 2, 5, and 10 mol% Mg are represented in Fig. 6 in the form of an Arrhenius plot of $\log K$ vs reciprocal of absolute temperature. The enthalpy of the reaction, ΔH , was obtained from the slope of the Arrhenius plot and was found to be 272 ± 16 kJ/mol. Within the limits of experimental error, ΔH showed no significant changes as the dopant concen-

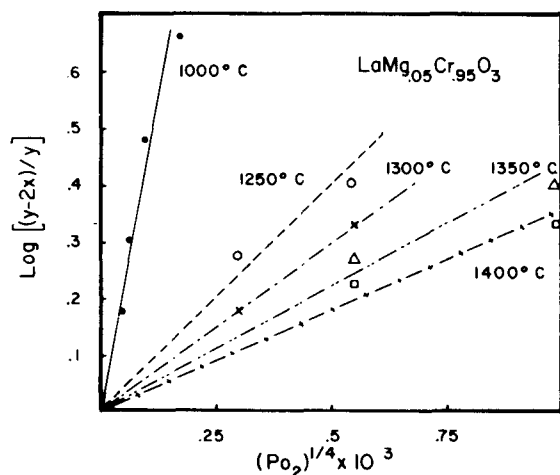


Fig. 5. Relative carrier concentration vs $P_{O_2}^{1/4}$ as a function of temperature for LaCrO_3 doped with 5 mol% Mg.

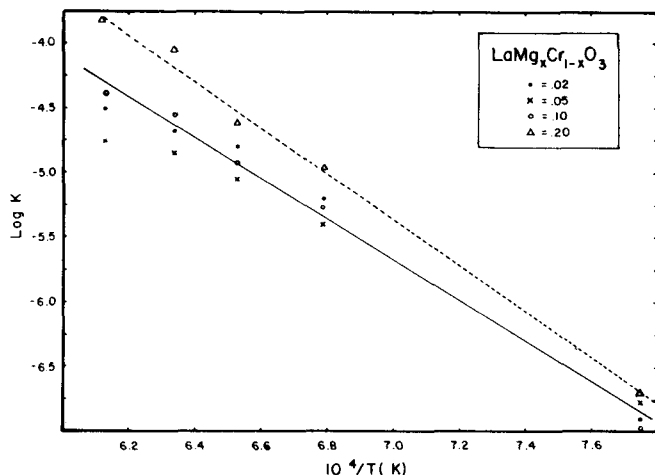


Fig. 6. Arrhenius plot of $\log K$ vs $1/T$, showing effect of dopant.

tration increased from 2 to 10 mol%. The free energy of formation of oxygen vacancies, ΔG , was accordingly represented by the general expression $\Delta G = [(272 \pm 16) - 0.08T]$ kJ/mol. The calculated ΔG values ranged from ≈ 169 to 136 kJ/mol at $T = 1287$ to 1640 K, respectively. On the other hand, the sample doped with 20 mol% Mg exhibited a behavior which is slightly different than that observed for lower dopant compositions, with a relatively lower ΔG value compared to those previously obtained. It is, therefore, concluded that ΔG is independent of composition up to 10 mol% Mg and shows a composition dependence beyond this dopant level. This suggests the exsolution of a second phase between 10 to 20 mol% MgO. Previous work¹⁵ indicates that the solubility limit of Mg in LaCrO_3 is about 15%.

An additional confirmation for the validity of the model is represented in Fig. 7 where $y - 2x$ is plotted as a function of $[\text{Mg}]^{1/2}$. For such a plot, Eq. (13) predicts a linear relationship at any given temperature and oxygen activity. This relationship is observed in Fig. 7 for compositions up to 10 mol% Mg. The deviation of the 20 mol% Mg-doped samples from linearity is probably due to the previously mentioned composition dependence where a second phase is exsolved. It is also of interest to note that extrapolation of the data in Fig. 7 to zero dopant concentration does not pass through the origin of the plot. In other words, even in the "Mg-free" LaCrO_3 sample, a residual acceptor dopant is present. Neutron activation analysis indicates that the level of acceptor impurities, such as Fe, Ca, and Cu, is sufficient to account for the observed nonzero extrapolation.

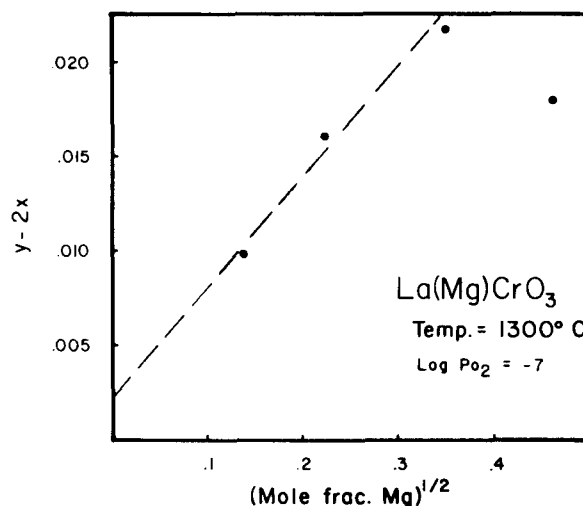


Fig. 7. Carrier concentration vs $[\text{Mg}]^{1/2}$ at 10^{-7} Pa and 1300°C .

V. Conclusions

The data obtained from TG experiments support the proposed defect model for the oxidation-reduction behavior of acceptor-doped LaCrO_3 . Both the TG data and proposed model indicate that at high P_{O_2} electronic compensation occurs by a $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$ transition, whereas ionic compensation takes place at lower P_{O_2} by the formation of oxygen vacancies. The oxygen activity at which electronic compensation shifts to ionic is both acceptor-dopant and temperature-dependent. The general behavior is that the transition shifts to higher oxygen activity as the temperature or the concentration of acceptor dopant increases.

The calculated data on free energy of formation showed no composition dependence doping up to 10 mol% Mg. For higher acceptor-dopant concentrations a composition dependence was observed.

References

- D. B. Meadowcroft, "Properties of Strontium-Doped Lanthanum Chromite," *Br. J. Appl. Phys.*, **2** [9] 1225-33 (1969).
- H. U. Anderson, R. Murphy, S. Semachaibovorn, B. Rossing, A. Aldred, W. Procarione, and R. Ackermann, "Electrical Conductivity, Volatilization and Preparation of LaCrO_3 Based Oxides," Conf. on High Temperature Science Related to Open-Cycle, Cool Fired MHD Systems, Argonne National Laboratory, Argonne, IL, April 1977.
- D. B. Meadowcroft and J. Wimmer, "Oxidation and Vaporization Processes in LaCrO_3 ," *Am. Ceram. Soc. Bull.*, **58** [6] 610-15 (1979).
- J. W. Halloran and H. U. Anderson, "Influence of P_{O_2} on Initial Sintering of Alpha Cr_2O_3 ," *J. Am. Ceram. Soc.*, **57** [3] 150 (1974).
- H. U. Anderson, "Influence of Oxygen Activity on the Sintering of MgCr_2O_4 ," *J. Am. Ceram. Soc.*, **57** [1] 34-37 (1974).
- G. Group and H. U. Anderson, "Densification of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$," *J. Am. Ceram. Soc.*, **59** [9-10] 449-50 (1976).
- H. U. Anderson, "Fabrication and Property Control of LaCrO_3 Based Oxides"; pp. 469-77 in *Processing of Crystalline Ceramics*. Edited by H. Palmour, R. Davis, and T. M. Hare. Plenum, New York, 1978.
- I. G. Austin and N. E. Mott, "Polarons in Crystalline and Non-Crystalline Materials," *Advan. Phys.*, **18** [71] 41-102 (1969).
- J. Faber, M. Mueller, W. Procarione, A. Aldred, and H. Knott, "Structural and Physical Properties of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ "; pp. 154-59 in *Conference on High Temperature Science Related to Open Cycle, Cool Fired MHD Systems*. Argonne National Laboratory, Argonne, IL, April 1977.
- H. U. Anderson, R. Murphy, K. Humphrey, B. Rossing, A. Aldred, W. Procarione, R. Ackermann, and J. Bates, "Influence of Composition and Cation Stoichiometry on the Volatility, Electrical Conductivity and Thermal Expansion of LaCrO_3 Based Oxides"; pp. 55-61 in *The Rare Earths in Modern Science and Technology*. Edited by G. J. McCarthy and J. J. Rhyne. Plenum, New York, 1978.
- D. B. Meadowcroft, "Some Properties and Applications of Strontium Doped Rare Earth Perovskites"; pp. 119-36 in *International Conference on Strontium Containing Compounds*. Edited by T. Gray. Atlantic Research Institute, Halifax, Canada, June 1973.
- F. A. Kröger and H. J. Vink, *Solid State Physics*, Vol. 3. Edited by F. Seitz and D. Turnbull. Academic Press, New York, 1965; p. 307.
- M. P. Pechini, "Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor," U. S. Pat. No. 3330697, July 1967.
- B. Flandermeyer, "Defect Chemistry of La-Doped SrTiO_3 ," M. Sc. Thesis, University of Missouri-Rolla, 1983.
- D. Schilling, "The Solubility of MgO in LaCrO_3 as a Function of Stoichiometry," M. Sc. Thesis, University of Missouri-Rolla, 1983.