Final Report

DEFECT CHARACTERIZATION OF ELECTRONIC
CONDUCTING PSEUDO-PEROVSKITE SYSTEMS

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I. Summary

The goal of the program has been to study the interrelationships between electrical conductivity, oxidation-reduction kinetics, defect structure, and composition of n- and p-type binary and ternary transition metal oxides. The stimulus for making these studies was the observation that both conducting n and p type oxides displayed a dependence on oxygen activity that was not predicted by the defect chemistry of their majority defects.

The project has focussed primarily on the understanding of electronic and ionic conduction in the $REBO_3$ oxides, where RE is a rare earth ion and B is a transition metal ion. This being done by studying the interrelationships between the electronic and ionic conductivity, the electronic structure of the B site transition metal ion, and the acceptor concentration. The dependence of these characteristics on the oxygen activity, the temperature, and the defect chemistry of the oxide system is being determined. Theoretical mechanisms and models are being developed from the body of experimental results to provide a predictive tool. The effect of dopants and impurities, processing, electrical and thermal stability as a function of oxygen activity and temperature and their relationship to defect chemistry of the perovskite type oxides have been studied extensively by this research team. Recent theoretical models have been developed to give qualitative interpretations of the observed data which would not be otherwise obtainable.

The experimental part of the investigation included specimen preparation thermogravimetric measurements, X-ray diffraction, thermally stimulated current, DTA/TGA, optical absorption, electrical conductivity, and Seebeck measurements.

The theoretical investigation involves modelling the electrical conductivity mechanisms utilizing the computation skills of Dr. Parris and his students.

This study is particularly addressing the trapping-to-precolation transition seen in many of our studies and disproportionation of the cations.

The main issue being addressed is how do transition metal oxides behave when subjected to high temperatures and variable oxygen activity? What are the relationships among electrical conductivity, oxidation-reduction state, defect structure, and composition for transition metal perovskites based on Cr, Mn, Fe, and Co? What are the roles of the transition metal ions and other crystallographic and thermodynamic factors that control the relative amounts of mixed ionic/electronic conductivity in perovskite type oxides?

Current studies show that donor doped n-type oxides and acceptor doped p-type oxides reversibly absorb or evolve oxygen in response to changes in oxygen activity. This is not the type of behavior that one would expect from the Verwey doping model. It also should be noted that, as acceptor doped p-type oxides lose oxygen, or donor doped n-type oxides absorb oxygen, the compensation mechanism changes from the electronic one predicted by Verwey to an ionic one. As a result of the difference in mobility between electronic and ionic defects, the electrical conductivity changes as the concentration of electronic defects changes. Thus, electrodes or resistors consisting of such oxides are susceptible to instabilities in resistance as they are cycled into temperature regimes where thermodynamic equilibrium may be attained. Many of the new energy conversion systems which use such oxides are encountering difficulties as a result of this instability in resistivity.

- The non-Verwey behavior is being studied in detail.

Questions being addressed are:

- 1) How does REBO_3 behave as $F(T, P_{\text{O}_2}, \text{compositions})$?
- 2) What are the relationships between defect structure, σ and redox state?
- 3) What are the factors that control mixed ionic/electronic conductivity?

- Many of these difficulties arise because some fundamental properties of the oxides are either not known or little understood. The problems depend on the particular application, but most can be categorized as:

- (1) inadequate characterization of the oxides, both chemically and structurally,
- (2) inadequate phase equilibria data, and
- (3) lack of defect chemistry data.

- This program is focussed on understanding the electrical behavior of perovskite type oxides as function of temperature, composition and oxygen activity.

The systems studied in approximately chronological order are:

$(\text{Ti}, \text{Nb})\text{O}_2$	$(\text{Ti}, \text{Al})\text{O}_2$
$(\text{BaLa})\text{TiO}_3$	$(\text{Sr}, \text{La})\text{TiO}_3$
$\text{La}(\text{Cr}, \text{Mg})\text{O}_3$	Li and Mg doped Cr_2O_3
$(\text{La}, \text{Mg})\text{MnO}_3$	$(\text{La}, \text{Sr})\text{MnO}_3$
$(\text{La}, \text{Nb})\text{CrO}_3$	$\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$
$(\text{La}, \text{Sr})(\text{Cr}, \text{Mn})\text{O}_3$	$(\text{Y}, \text{Ca})\text{CrO}_3$
$(\text{La}, \text{Ca})(\text{Mn}, \text{Al})\text{O}_3$	$(\text{Y}, \text{Ca})\text{MnO}_3$
$(\text{La}, \text{Ca})\text{MnO}_3$	$(\text{La}, \text{Ca})(\text{Cr}, \text{Co})\text{O}_3$
$(\text{La}, \text{Ca})(\text{Cr}, \text{Al})\text{O}_3$	$(\text{La}, \text{Ca})(\text{Ni}, \text{Fe})\text{O}_3$

The major results and accomplishments obtained with these studies are:

- Redox behavior studies of $(\text{La}, \text{Ca}, \text{Sr})(\text{Cr}, \text{Nb}, \text{Mg})\text{O}_3$ completed. (Oxygen exchange dominated by grain boundaries; p-n transition observed for $\text{La}(\text{Cr}, \text{Nb})\text{O}_3$).
- Redox behavior studies of $(\text{La}, \text{Ca}, \text{Sr})\text{MnO}_3$ completed. (Disproportionation of $2\text{Mn}^{+3} \rightleftharpoons \text{Mn}^{+4} + \text{Mn}^{+2}$ explained).
- Redox behavior studies of $(\text{Y}, \text{Ca})\text{CrO}_3$ completed. (YCrO_3 more stable than LaCrO_3).
- Behavior of $(\text{La}, \text{Sr})(\text{Mn}, \text{Cr})\text{O}_3$ explained by a Trapping - Percolation model.
- Air sinterable LaCrO_3 model.
- Behavior of $(\text{Y}, \text{Ca})\text{MnO}_3$ and $(\text{La}, \text{Ca})\text{MnO}_3$ modelled by small polaron hopping mechanism and Mn disproportionation.

- Behavior of $(\text{La,Ca})(\text{Al,Mn})\text{O}_3$ modelled by small polaron hopping mechanism combined with Mn disproportionation and site percolation.
- Trapping - Percolation conductivity model developed.
- Transition metal cation disproportionation used to explain behavior of LaMnO_3 , YMnO_3 , LaCoO_3 and Fe containing perovskites.

The results from this program have increased our understanding of the defect structure and electrical conductivity mechanisms of these systems. This is aiding DOE in meeting some of its mission of improving the utilization of our energy resources in an environmentally sound way because a number of these goals utilize oxides as part of the solution. A few of the applications are:

- Fuel Cells
- Oxygen Separation
- Gas Ignitors
- High Temperature Electrodes
- Catalysis Applications
- Sensors
- High Temperature Superconductors

Some of these applications are encountering difficulties because the chosen oxides are either changing properties or interacting with other components during use.

II. Current Project Overview

A. Specific project objectives

This program has been in place since July 1, 1985 (DE-FG 0285 ER 45219) and is an extension of a previous program (DE-AC02 80ER10598) which was initiated in mid 1980. Since the beginning of the initial program the overall goals have not changed except with some of the measurements and the particular oxides being studied.

The goal of the program has been to study the interrelationships between electrical conductivity, oxidation-reduction kinetics, defect structure, and composition of n- and p-type binary and ternary transition metal oxides. The stimulus for making these studies was the observation that both conducting n and p type oxides displayed a dependence on oxygen activity that was not predicted by the defect chemistry of their majority defects. The experimental part of the investigation included specimen preparation, thermogravimetric measurements, X-ray diffraction, thermally stimulated current, oxygen diffusion, optical absorption, transmission electron microscopy, electrical conductivity, and Seebeck measurements. The system studied approximately in chronological order are: $(\text{Ti,Nb})\text{O}_2$, $(\text{Ti,Al})\text{O}_2$, $(\text{BaLa})\text{TiO}_3$, $(\text{Sr,Lu})\text{TiO}_3$, $\text{La}(\text{Cr,Mg})\text{O}_3$, Li and Mg doped Cr_2O_3 , $(\text{La,Mg})\text{MnO}_3$, $(\text{La,Sr})\text{MnO}_3$, $(\text{La,Nb})\text{CrO}_3$, $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$, $(\text{La,Sr})(\text{Cr,Mn})\text{O}_3$,

(Ya,Ca)CrO₃, (La,Ca)(Mn,Al)O₃, (Y,Ca)MnO₃, (La,Ca)MnO₃, (La,Ca)(Cr,Co)O₃, (La,Ca)(Cr,Al)O₃, and (La,Ca)(Ni,Fe)O₃.

B. Current objectives

The objective of this project is to understand electronic and ionic conduction in the REBO₃ oxides, where RE is a rare earth ion and B is a transition metal ion. This is being done by studying the interrelationships between the electronic and ionic conductivity, the electronic structure of the B site transition metal ion, and the acceptor concentration. The dependence of these characteristics on the oxygen activity, the temperature, and the defect chemistry of the oxide system is being determined. Theoretical mechanisms and models are being developed from the body of experimental results to provide a predictive tool.

The principal investigators bring a wide base of theoretical and experimental skill to the proposed work. The effect of dopants and impurities, processing, electrical and thermal stability as a function of oxygen activity and temperature and their relationship to defect chemistry of the perovskite type oxides have been studied extensively by this research team. Recent theoretical models have been developed to give qualitative interpretations of the observed data which would not be otherwise obtainable.

The immediate goals are:

- 1) To perform studies which will further confirm the existence of Mn⁺²/Mn⁺⁴ pairs in LaMnO₃ or other Mn containing perovskites. Such pairing was proposed to explain the observed experimental results for (La,Sr)(Cr,Mn)O₃.
- 2) To perform studies which will characterize the regions of mixed conductivity in the systems we have already studied, e.g., LaCrO₃, LaCoO₃ and LaMnO₃. The results of the proposed studies, combined with information on electronic structure and thermodynamic properties, will be used to develop new oxide systems in which the mixed conductivity can be systematically controlled for "tailored" applications. This can be done by making the proposed studies, which will yield the required fundamental information.

C. Planned future work

The goals through June 30, 1994 are:

- 1) to complete the studies on the (La,Ca)CoO₃ system which S. Sehlin is conducting. These studies are giving us insight into the disproportionation of Co ions.
- 2) to complete the studies on the (La,Ca)(Cr,Al)O₃ system which J. Conrad is conducting. His work is allowing testing of the theoretical models of Drs. Parris and Sparlin. It appears that long range hopping through the Cr sites is of much greater importance than we originally thought.
- 3) to complete the studies that M. Etchemendy is making on the (La,Ca)(Ni,Fe)O₃ system. It appears that his results are consistent with disproportionation of Fe⁺⁴ to Fe⁺³ and Fe⁺⁵.
- 4) to complete the modelling studies of B. Bookout. These studies are leading us to a model which can explain our data on the (La,Ca)(Cr,Al)O₃, (La,Ca)(Mn,Al)O₃ and

(La,Sr)(Cr,Mn)O₃ systems. This model will allow us to have a basis for predictions of behavior in other systems.

- 5) to initiate and complete a study in the (La,RE)(Cr,Al)O₃ system. In this study the rare earth (RE) substituting for La will be varied and the change in hopping properties will be studied as a function of ionic radii of the rare earth.
- 6) to continue our studies in the regions where mixed conductivity is important. We expect to measure ionic transport numbers for some of our chromite systems in the reducing regions where oxygen vacancies are becoming a major feature of the defect structure. The models that we have proposed to explain the redox behavior of LaCrO₃, LaMnO₃, YCrO₃, BaTiO₃ and SrTiO₃ include oxygen activity and temperature regimes where ionic compensation becomes important, as is apparent from the electrical neutrality conditions. We expect to verify the existence and magnitude of the ionic transport processes when these regimes are explored more fully. Our preliminary data suggest that mixed conductivity is occurring in these critical regions. We are initiating a systematic study to define the regions of mixed conductivity in a number of perovskite type materials. Such information is very important for catalyst, solid oxide fuel cell and oxygen delivery system applications.

D. How this project relates to the DOE program's mission

The utilization of oxides for energy related applications require a detailed understanding of the defect structure of the oxides and a knowledge of how the defect structures change with the application environment.

The results of our current and previous investigations, are proving to be very useful and relevant to the utilization of the transition metal oxides. Our results are currently most useful in catalysis, in fuel cell electrodes, in thermoelectrical power, in ceramic capacitor dielectrics, and in superconducting oxides.

E. Relationships to other DOE projects

The following listing of laboratories and our interaction with them came about because of the success of our current and past DOE supported research program. Materials and processes discovered under research funding attract defense agencies with applied problems in search of materials solutions.

California Institute of Technology, Jet Propulsion Laboratory (JPL)

The personnel at JPL are interested in the results of our program with respect to materials applications in thermoelectric power and oxygen pump technology. We have supplied JPL with materials and consultation for their particular needs.

Allied Signal/Air Research

Garrett is using both the results of our work and the materials we have developed in their multilayer high temperature fuel cell program.

Argonne National Laboratory (ANL)

The personnel at ANL have a high temperature fuel cell program in which they are making

use of the results of our program. We are supplying both consultation and materials to this program. We have worked closely with Drs. Balachandran and Dorris to develop materials for their solid oxide fuel cell program. Also we have a student doing part of his Ph.D. program using ANL facilities.

DOE/Morgantown

We have a program with DOE-METC which is directed at developing materials which will have superior properties for cathode applications for fuel cells than the oxide currently being used.

Oak Ridge National Laboratories

We have been collaborating with ORNL - Solid State Division for several years. Exchange visits were made possible through Oak Ridge Associated University Programs. Electron paramagnetic resonance and EMF cell measurements were conducted on our samples at ORNL.

Ceramtec, Inc.

We are helping Ceramtec develop air sinterable interconnects for their planar solid oxide fuel cell program.

F. Major recent accomplishments of current program

1. Defect structure studies of LaCrO_3 have shown that it is possible to make n-type LaCrO_3 by Nb-doping. These studies indicate that this material conducts via a small polaron mechanism with an electron and hole mobility of about 0.002 and 0.05 $\text{cm}^2/\text{v-sec}$ respectively over the temperature range between 1100 and 1300°C. [J. Solid State Chem. 78 242-249 (1989)].
2. The redox kinetics of Sr-doped LaCrO_3 and La-doped SrTiO_3 were determined from weight change and electrical conductivity measurements. Both studies indicate that the oxygen exchange is very rapid. The oxygen exchange can be divided into grain boundary chemical diffusion and volume chemical diffusion portions whose coefficients and activation energies at 1000°C are about 10 cm^2/sec and 4500 cal/mol and 30000 cal/mol respectively. [J. Amer. Cer. Soc. 70 C189-193 (1987)].
3. Undoped LaMnO_3 , Sr-doped LaMnO_3 and Mg-doped LaMnO_3 showed reversible oxidation-reduction behavior. Phase stabilities for these oxides were determined. The results show that both Sr and Mg doping cause the LaMnO_3 to dissociate at higher oxygen activities than for undoped LaMnO_3 . The small polaron hopping model was used to interpret the electrical and Seebeck data. The results suggested that the (hole) conductivity for these perovskites was dominated by the mobility rather than by the carrier concentration. This implies that defect related traps dominate the conduction process. [J. Solid State Chem. 87 55-63 (1990)].
4. The studies of the $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ system have shown that the conduction processes (metallic or small polaron) have little temperature dependence and are almost entirely a function of oxygen stoichiometry. The ability to achieve superconductivity is so dependent on oxygen stoichiometry that it is not possible to process this oxide and obtain superconductivity without subsequent oxygen anneals in the 400 to 700°C temperature range. [MRS 99 (1988)].
5. The substitution of 10 to 20 m% Ca and Co into LaCrO_3 has enabled the system to be sintered to .95% TD at 1400°C without deterioration of either the electrical conductivity or high

temperature stability of the resulting dense ceramics. These sinterable LaCrO_3 based oxides have immediate applications as solid oxide fuel cell (SOFC) cathodes and interconnects. These studies were transferred to SOFC programs sponsored by DOE-Morgantown Energy Technology Center (METC), ANL and Ceramatec, Inc. [J. of the European Cer. Soc. 9 285-292 (1992)].

6. The substitution of 10 to 20 m% Ca and Co into YCrO_3 enables densification in air at temperatures below 1450°C . This is a significant accomplishment for which a patent disclosure has been made. Application of this technology has been used in our SOFC program sponsored by DOE-METC. [2nd Intl. Symp. on Solid Oxide Fuel Cells, ed. Singhal, Electrochem. Soc. (1991)].

7. A study of structure of the high temperature (1400°C) phases of La substituted SrTiO_3 has demonstrated our ability to determine small changes in structure as well as to determine cation defect concentrations using X-ray powder diffraction methods. In this study we were able to show that the oxidized state of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ contained cation vacancies. This is the first direct evidence regarding the defect structure of this system. [JAP 65 1492-1498 (1989)].

8. The studies in the $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ system also are yielding some important results. They are showing that this oxide system is more stable towards reduction than LaCrO_3 . This suggests that we may have an alternate to LaCrO_3 as a high temperature electrode. Some of the other significant results found for the YCrO_3 system are:

- a) $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ conducts via the adiabatic small polaron mechanism. It fits this mechanism better than any oxide that we have found either in the literature or in our previous measurements.
- b) With the appropriate additions of Ca and Co, YCrO_3 can be densified in air at temperatures below 1450°C without degradation of stability towards reduction.
- c) The thermal expansion coefficient can be increased from 7.7 to $9.5 \times 10^{-6}^\circ\text{C}^{-1}$ by addition of 0 and 20 mol% Ca respectively.

[J. Solid State Chem. 94 329 (1991); Solid State Ionics 49 223 (1991)].

9. The studies on the $(\text{La}, \text{Sr})(\text{Mn}, \text{Cr})\text{O}_3$ system have yielded some significant results which are significantly increasing our understanding of the conduction behavior of perovskite oxides. the results are:

- a) conduction occurs via the nonadiabatic small polaron mechanism.
- b) the Seebeck data suggest that $(\text{La}, \text{Sr})\text{MnO}_3$ contains $\text{Mn}^{+2} - \text{Mn}^{+4}$ pairs which dominate the electrical conductivity. Our data are consistent with 50% of the Mn being in the +4 state with little dependence on Sr content.
- c) The electrical conductivity suggests that it depends upon Mn content. At Mn concentrations less than 10 mol%, the Mn acts as traps for the carriers and the room temperature conductivity decreases by 2 to 3 orders of magnitude. As the Mn content increases to 30 mol% and beyond, the conduction increases hypercolation through the 3d band of the Mn.

[Phy. Rev B 43 7991-7999 (1991)].

10. The studies on the $(\text{La,Ca})(\text{Al,Mn})\text{O}_3$ system show that the conductivity can be related to a site percolation-type model in which small polarons hop between degenerate Mn sites. Conductivity below the percolation limit is very low and can be attributed to either longer than nearest neighbor hopping or ionic conductivity, while conductivity above the percolation limit increases dramatically due to a connecting path of available Mn sites which span the crystal. The increase in activation energy for lower Mn concentration, along with a systematic increase in Seebeck coefficient with decreasing Mn content, seems to imply the suppression of $\text{Mn}^{2+} - \text{Mn}^{4+}$ disproportionation (pairing) through a dependence of site energy upon adjacent site occupancy. [Cer. Transation Vol. 24, Amer. Cer. Soc., ed. Mason & Routbort, 1990 p. 229].

11. The studies on the $(\text{Y,Ca})(\text{Mn})\text{O}_3$ and $(\text{La,Ca})\text{MnO}_3$ systems showed that the electrical conduction appeared to occur via a small polaron hopping mechanism for both systems. Seebeck coefficient data did not support the traditional assumption that Mn is present in Mn perovskites only in the +3 and +4 valence states. The Seebeck data could be explained by allowing for the presence of site-blocking divalent Mn cations; accordingly a new defect model was developed which included the thermally excited disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+} pairs. Since compositions in $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ exhibited very slight oxygen activity-dependent behavior as ambient oxygen activity was reduced, several compositions in the system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ were studied in order that the defect model could be applied to the oxygen-dependent region in manganites. The model was successful in explaining the experimentally observed dependence of oxygen stoichiometry, electrical conductivity, and Seebeck coefficient upon ambient oxygen activity. [J. Solid State Chem. 102 175-184 (1993); J. Solid state Chem. 102 184-192 (1993)].

12. The studies in the $(\text{La,Ca})(\text{Cr,Al})\text{O}_3$ system are yielding some important results. They are showing that the conductivity can be related to a site percolation-type model which involves the motion of small polarons through both short and long range hopping through the Cr sites. This differs from the case of $\text{La}(\text{Cr,Mn})\text{O}_3$ [Phys. Rev. Letters 65, 1383 (1990); Phys. Rev. 13, 43 7991 (1991)] where the conductivity occurs by hopping through nearest neighbor the Mn and Cr sites.

13. The studies on the densification of $(\text{La,Ca})\text{CrO}_3$ show that densities greater than 93% of theoretical density can be achieved in air in the 1400-1500°C range for 20-30 m% Ca content. Densification occurs via a transient liquid phase resulting from the incongruent melting of CaCrO_4 at 1022°C. As densification proceeds the liquid phase is reabsorbed into the solid $(\text{La,Ca})\text{CrO}_3$ phase. Since a homogeneous distribution of the liquid phase is required for good densification, the initial distribution of LaCrO_4 in $(\text{La,Ca})\text{CrO}_4$ within the starting powder is extremely important. The results show that when the $(\text{La,Ca})\text{CrO}_3$ compositions are initially prepared, $(\text{La,Ca})\text{CrO}_4$ forms. The chromite subsequently decomposes to $(\text{La,Ca})\text{CrO}_3$ and CaCrO_4 at 700°C. It is the distribution of this CaCrO_4 that needs to be carefully controlled. [3rd Intl. Symp. on SOFC, ed. Singhal, Electrochem Soc. (1993)].

14. The electrical conductivity and thermopower studies on the $(\text{La,Ca})\text{CoO}_3$ system have shown that the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ compounds are p-type small polaron conductors. $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ compounds are also believed to be small polaron conductors at room temperature for $x \leq 0.20$ with a higher conductivity than the corresponding chromites. Unexpectedly, for compositions in the mixed system containing 10 mol% and 20 mol% Ca, the conductivity for Co-rich compositions is lower than that of Cr-rich compositions at room temperature. At higher temperatures the conductivity increases with increasing Co content. The thermopower can be interpreted using Heikes's formula and a mechanism of thermally activated disproportionation among Co ions.

A model was developed which provides a plausible fit to the temperature dependence of the conductivity and thermopower of LaCoO_3 . The crystal field energy is slightly larger than the exchange energy, resulting in $S=0$ for trivalent Co ions at low temperature. Higher spins are achieved by thermal activation of electrons from the t_{2g} to the e_g state. Other investigators have suggested that the expected intermediate spin ($S=1$) state is unstable, and that the high spin ($S=2$) state is predominant at high temperatures. The disproportionation of high spin Co^{3+} into high spin Co^{2+} and Co^{4+} is proposed to account for the electrical properties of LaCoO_3 . [J. Matl. Sci. 27 5477-5482 (1992); Cer. Trans., Vol. 24, ed. Mason & Routbort, Amer. Cer. Soc. (1990) p. 249].

G. Submitted publications from project (since 1985)

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P.E. Parris and B.D. Bookout, "Energy-Projected Effective Medium Theory of Long-Range Hopping on Energetically Disordered Lattices", Phys. Rev. B 48, 9354 (1993).

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B.D. Bookout and P.E. Parris, "Long-Range Random Walks on Energetically Disordered Lattices", Phys. Rev. Letters 71 16 (1993).

D.M. Sparlin and R.P. Raffaele, "Compensation in the RMO_3 Perovskite Structure", Point Defects and Related Properties of Ceramics, ed. T.O. Mason and J.L. Routbort, Ceramic Transactions, Vol. 24, Amer. Cer. Soc. (1991) p. 221.

J.D. Carter, V. Sprenkle, M.M. Nasrallah and H.U. Anderson, "Solubility of Calcium in Lanthanum Chromite", 3rd International Symposium in Solid Oxide Fuel Cells, May 16-21, 1993, Honolulu, Hawaii.

J.W. Stevenson, M.M. Nasrallah, H.U. Anderson, and D.M. Sparlin, "Defect Structure of $\text{Y}_{1-y}\text{Ca}_y\text{MnO}_3$ and $\text{La}_{1-y}\text{Ca}_y\text{MnO}_3$ I: Electrical Properties", J. Solid State Chem., 102, 175-184, 1993.

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R. Koc and H.U. Anderson, "Liquid Phase Sintering of LaCrO_3 ", J. of the European Cer. Soc., 9, 285-292, 1992.

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H.U. Anderson, "Review of P Type Doped Perovskite Materials for SOFC and Other Applications", Solid State Ionics, 52 33 (1992).

S.A. Howard, J-K Yau and H.U. Anderson, "X-ray Powder Diffraction Structural Phase-Transition Study of $\text{La}(\text{Cr}_{1-x}\text{Mn}_x)\text{O}_3$ ($y = 0$ to 0.25) Using the Rietveld Method of Analysis", J. Amer. Cer. Soc., 75 1685-1687 (1992).

R. Koc and H.U. Anderson, "Electrical Conductivity and Seebeck Coefficient of $(\text{La,Ca})(\text{Cr,Co})\text{O}_3$ ", *J. Materials Sci.*, 27 5477-5482 (1992).

R. Raffaele, H.U. Anderson, D.M. Sparlin and P.E. Parris, "Transport Anomalies in the High Temperature Hopping Conductivity and Thermopower of Sr-Doped $\text{La}(\text{Cr,Mn})\text{O}_3$ ", *Phy. Rev.* 8 43, 7991-7999 (1991).

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M. DeBarr, P.E. Parris, D.M. Sparlin and H.U. Anderson, "Conduction Mechanism in the $\text{La}(\text{Mn,Al})\text{O}_3$ Series", *ibid.* p. 229.

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M.M. Nasrallah, H.U. Anderson and J. Stevenson, "Defect Chemistry and Properties of $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ ", 2nd International Symposium on Solid Oxide Fuel Cells, Athens, Greece, July 2-5, 1991, ed. S. Singhal, *Electrochem. Soc.*, Pennington (1991).

R. Raffaele, H.U. Anderson, D.M. Sparlin, and P.E. Parris, "Evidence for a Crossover from Multiple-Trapping to Percolation in the High Temperature Conductivity of Mn-Doped LaCrO_3 ", *Phys. Rev. Letters* 65, 1383 (1990).

J.H. Kuo, H.U. Anderson and D.M. Sparlin, "Oxidation-Reduction Behavior of Undoped and Sr Doped LaMnO_3 : Defect Structure, Electrical Conductivity and Thermoelectric Powers", *J. Solid State Chem.*, 87, 55-63 (1990).

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H.U. Anderson, M.M. Nasrallah, F.D. Blum and M.S. Smith, "Polymeric Synthesis of Perovskite Powders and Films", *Proc. of Intl. Conf. on the Chemistry of Electronic Ceramic Mat'l's*, NIST 1990, Eds. R. Roth, P. Davies and R. Cava.

S.A. Howard, J.K. Yau and H.U. Anderson, "Structural Characteristics of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3+\delta}$ as a Function of Oxygen Partial Pressure at 1400°C", *J. Appl. Phys.*, **65** (4), 1492-1498 (1989).

R. Koc, H.U. Anderson, S.A. Howard and D.M. Sparlin, "Structural, Sintering and Electrical Properties of the Perovskite Type $(\text{La},\text{Sr})(\text{Cr},\text{Mn})\text{O}_3$ ", *Proc. of the 1st Intl. Symp. on Solid Oxide Fuel Cells*, Ed. S.C. Singhal, Electrochem Soc., 220-242, 1989.

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C.J. Yu, H.U. Anderson and D.M. Sparlin, "High-Temperature Defect Structure of Nb-Doped LaCrO_3 ", *J. of Solid State Chem.*, **78**, pp. 242-249, (1989).

R.F. Huang and H.U. Anderson, "Effect of Volatilization on the Conduction Behavior of Acceptor-Doped Chromium Oxide", *J. Am. Cer. Soc.*, **72** (8), pp. 1382-85, (1989).

H.U. Anderson, C. Brannon and D.M. Sparlin, "Thermogravimetric Studies on $\text{Ba}_2\text{YCu}_3\text{O}_7$ ", *Mat. Res. Soc.*, **99**, April 1988.

C.J. Yu, D.M. Sparlin and H.U. Anderson, "Oxidation Kinetics of Polycrystalline LaCrO_3 ", *J. Am. Cer. Soc.*, **70** C189-192 (1987).

H.U. Anderson, M.M. Nasrallah, B.K. Flandermeyer and A.K. Agarwal, "High Temperature Redox Behavior of Doped SrTiO_3 and LaCrO_3 ", *J. Solid State Chem.*, **56**, 325 (1985).

B.K. Flandermeyer, M.M. Nasrallah, D.M. Sparlin and H.U. Anderson, "Thermogravimetric and Electrical Conductivity Studies of Mg Doped LaCrO_3 and La-Doped SrTiO_3 ", in Transport in Nonstoichiometric Compounds, Ed. Simkovich and Stubican, Plenum, 1985.

B.K. Flandermeyer, M.M. Nasrallah, D.M. Sparlin and H.U. Anderson, "High Temperature Stability of Magnesium Doped Lanthanum Chromite", *High Temp. Sci.*, **20** 259 (1985).

H. Principal personnel

- 1) Dr. H.U. Anderson, Curators' Professor of Ceramic Engineering and Senior Investigator, Materials Research Center, Principal Investigator.

A. Role in project

His responsibilities are to act as program director and to give guidance in the ceramic powder processing and the defect chemistry.

B. *Principal areas of research and expertise*

Defect chemistry and nonstoichiometry of oxides; sintering behavior of oxides and metals; electrical degradation of dielectrics; methods of preparing high purity oxides from organometallics; titanates for use as capacitors and resistors; corrosion of ceramics; perovskites and spinels for use as high temperature electrodes, insulators and catalysts; processing of ceramic materials; multilayer substrates and capacitors; preparation of thin film oxides.

C. *Percentage of time devoted to project*

- 1) Academic year 10%
- 2) Summer 2 months (100%)
~ 20% Calendar year

D. *Education*

B.S., Ceramic Engineering, University of Utah, 1957
Ph.D., Engineering Science, University of California-Berkeley, 1962

E. *Professional experience*

Associate Professor to Professor of Ceramic Engineering, UMR, 1970-present
Associate Professor, Oregon Graduate Center, Beaverton, Oregon, 1968-70
Senior Chemist, Sprague Electric Co., North Adams, Massachusetts, 1962-68

F. *Professional activities & honors*

Fellow, American Ceramic Society, 1979
Faculty Excellence Award, 1987 and 1988
Curators' Professor, December 1988
Editor, J. American Ceramic Society, 9/92 - present
Member Ad Hoc Technical Panel to Advise DOE-Transportation on development of a National Program Plan for Fuel Cell in Transportation 2/92 - present

Patents:

James E. Schroeder & Harlan U. Anderson, "Multilayer Ceramic Oxide Electrolyte for Fuel Cells and Electrolysis Cells", U.S. Patent #5,057,362, October 15, 1991.

J.E. Schroeder and H.U. Anderson, "Multilayer Ceramic Oxide Solid Electrolyte for Fuel Cells and Electrolysis Cells and Method for Fabrication Thereof", US Patent #4,957,673, Sept. 18, 1990.

B.K. Flandermeyer, R.B. Poeppel, J.T. Dusek and H.U. Anderson, "Sintering Aid for Lanthanum Chromite Refractories", US Patent #4,749,632, 1988.

W.J. Brady and H.U. Anderson, "Method and Composition for Producing Hard Surface Carbide Insert Tools", US Patent #4,682,987, July 28, 1987.

R.B. Amin, H.U. Anderson, C-E. Hodgkins, "Multilayer Ceramic Capacitors Using LiF as Sintering Aid", US Patent #4,082,906, April 1978.

G. *Relevant (not from project) publications*

N.G. Eror and H.U. Anderson, "Polymeric Precursor Synthesis of Ceramic Materials", Proc. Better Ceramics Through Chemistry II, Matls. Res. Soc., 73, 1987.

J.P. Guha and H.U. Anderson, "Processing-Property Relations of Perovskite Based Solid Solutions in the System $\text{PbO-Fe}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-WO}_3$ ", Ceramic Powder Processing Science III, Ed. G.L. Messing, S. Hirano and H. Hausner, Vol. 12, Ceramic Transactions, Amer. Cer. Soc., 1990, p. 709.

H.U. Anderson, C.C. Chen and J.C. Wang, "Synthesis of Conducting Oxide Films and Powders from Polymer Precursors, *ibid*, p. 749.

H.U. Anderson, M.M. Nasrallah, F.D. Blum and M.S. Smith, "Polymeric Synthesis of Perovskite Powders and Films", Proc. of Intl. Conf. on the Chemistry of Electronic Ceramic Matl's, NIST 1990, Eds. R. Roth, P. Davies and R. Cava.

C.C. Chen, M.M. Nasrallah and H.U. Anderson, "Preparation and Electrode Characteristics of Dense $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ Thin Film by Polymeric Precursors", 3rd International Symp. on Solid Oxide Fuel Cells, Proceedings Vol. 93-4, Electrochem Soc., Eds., S.C. Singhal & H. Iwahara, pp. 252-267, 1993.

- 2) Collaborator: Don M. Sparlin
Professor

Organization: University of Missouri-Rolla, Physics Department

A. *Role in the project*

To oversee the design of experiments and the computer analysis of data generated by group projects. To collaborate with students and interested faculty in the creation of models applicable to electronic and ionic transport in the perovskite based conducting ceramics.

B. *Principal areas of research and expertise*

Electronic and computer based instrumentation. Modelling and analysis of data.

C. *Percentage of time devoted to project*

1)	Academic year	5% (non DOE funded)
2)	Summer	1 month (11%)

D. *Education*

B.S., Engineering Physics, Kansas University, 1959
Ph.D., Physics, Northwestern University, 1964

E. *Professional experience*

29 years experience in academic research and teaching

20 years experience in electronic instrumentation
 10 years affiliation with the Center for Electronic Materials

F. Professional activities & honors

6 consecutive UMR Faculty Excellence Awards for teaching/research/service.
 Outstanding Poster at the 1988 Metallurgical Society Meeting (instrumentation contribution).

- 3) Collaborator: Paul E. Parris
 Associate Professor

Organization: University of Missouri-Rolla, Physics Department

A. Role in the project

To apply theoretical models of hopping conduction in disordered systems to the analysis of electrical conduction and thermoelectric power data generated by project members, and to guide the choice of new materials to explore for purposes of comparison with existing theoretical models.

B. Principal areas of research expertise

Theoretical expertise in the area of transport and relaxation processes in disordered solids, including hopping conduction, trapping kinetics, and quantum localization.

C. Percentage of time devoted to project

1)	Academic year	5% (non DOE funded)
2)	Summer	1 month (11%)

D. Education

B.S., Physics, George Mason University, 1980
 M.A., Physics, University of Rochester, 1982
 Ph.D., Physics, University of Rochester, 1994

E. Professional experience

Associate Professor of Physics, University of Missouri-Rolla, 1992-present
 Assistant Professor of Physics, University of Missouri-Rolla, 1986-93
 Postdoctoral Associate, Massachusetts Institute of Technology, 1984-86

F. Professional activities & honors

Two-time recipient of the University of Missouri-Rolla Faculty Excellence Award
 Member of the American Physical Society
 Chaired Sessions of the March Meeting of the American Physical Society

G. *Relevant (not from project) publications*

P.E. Parris,, "Quantum and Stochastic Aspects of Low-Temperature Trapping and Reaction Dynamics", J. of Statistical Physics, 483, 1161, (1991).

P.E. Parris, and J.Wm. Edwards, "Exciton Trapping Dynamics at Very Low Temperatures", J. of Luminescence, 45, 279 (1990).

P.E. Parris, "Long-Range Hopping in Substitutionally Disordered Solids", Physical Review, B39, 9343 (1989).

P. Phillips, K. Kundu, D.H. Dunlap and P.E. Parris, "A New Look at Hopping, Trapping, and Localization", in Disorder and Nonlinearity, ed. by A.R. Bishop, D.K. Campbell and St. Pnevmatikos (Springer, Berlin, 1989).

P.E. Parris, "One-Dimensional Trapping Kinetics at Zero Temperature", Physical Review Letters, 62 1392 (1989).

P.E. Parris, "One-Dimensional Quantum Transport in the Presence of Random Traps", Physical Review B40, 4928 (1989).

J. Wm. Edwards and P.E. Parris, "Quantum Transport in the Presence of Random Traps", Rapid Communication, Physical Review B40, 8045 (1989).

P.E. Parris, "Exciton Diffusion at Finite Frequency: Luminescence Observables for Anisotropic Percolating Solids", J. Chemical Physics, 90, 2416 (1989).

- 4) Collaborator: Magdi M. Nasrallah
Professor of Materials Science and Engineering at Cairo University in Egypt
Research Professor of Ceramic Engineering

Organization: University of Missouri-Rolla

A. *Role in the project*

Dr. Nasrallah returned to our research group as a visiting professor in July 1989. He is assisting with experimental details for the ionic conductivity experiments, and guiding the interpretation of results. He is experienced in ESR and NMR studies of transition metal oxides and in defect chemistry modeling.

B. *Principal areas of research and expertise*

Synthesis and Properties of Ceramics and Glasses; Building Materials; Nonstoichiometry and Defect Chemistry; Gas-Solid reactions; Perovskites for Solid Oxide Fuel Cells; Mixed Conductivity for electrode and Catalysis applications.

C. *Percentage of time devoted to project*

- 1) Academic year 20% (non DOE funded)

D. *Education*

B.Sc. (Hons.), Applied Chemistry, Cairo University, 1965
 M.Sc., Solid State Science, American University of Cairo, 1968
 Ph.D., Materials Engineering, University of California, LA, 1972

E. *Professional experience*

Professor of Materials Engineering, Metallurgy Department, Faculty of Engineering, Cairo University, 1984-present.
 Research Professor, Ceramic Engineering, University of Missouri, U.S.A., 1989-present.
 Associate to Professor, Materials Engineering, American University in Cairo, 1977-1986 (Part time).
 Associate Professor, Metallurgy Department, Faculty of Engineering, Cairo University, 1978-1983.
 Research Associate Professor, Department of Ceramic Engineering, University of Missouri-Rolla, 1981-1984.
 Assistant Professor, Metallurgy Department, Faculty of Engineering, Cairo University, 1975-1978.
 Assistant Professor, Materials Engineering Department, School of Engineering, Pahlavi University, Iran, 1973-1975.

F. *Professional activities & honors*

Award in Recognition of Outstanding Academic Record, Cairo University, 1965
 Graduate Fellowship, The American University of Cairo, 1967
 National Merit Award, Academy of Science, 1985
 Member of the American Ceramic Society; National Institute of Ceramic Engineers; Electrochemical Society; and the Egyptian Corrosion Society

G. *Relevant (not from project) publications*

C.C. Chen, M.M. Nasrallah, H.U. Anderson and W.J. James, "Formation and Characterization of Zirconium Dioxide Films by Plasma-Enhanced Chemical Vapor Deposition", Proc. 9th Symp. Plasma Process, Electrochem. Soc. 1992, pp. 624-635.

C.C. Chen, M.M. Nasrallah and H.U. Anderson, "Cathode/Electrolyte Interactions and Their Expected Impact on SOFC Performance", Proc. 3rd International Symposium on Solid Oxide Fuel Cells, Honolulu, May 1993.

C.C. Chen, M.M. Nasrallah and H.U. Anderson, "Synthesis and Characterization of YSZ Thin Film Electrolyte", Proc. 9th Intl. Conf. on Solid State Ionics, Netherlands, September 1993.

M.M. Nasrallah, S.K. Arif and A.M. Bishay, "Conductivity, Mossbauer and Electron Spin Resonance of Iron in Silicate Glass", Mat. Res. Bull., 19, 269-277 (1984).

M.M. Nasrallah and R.A. Weeks, "Constraints on the Fusion Processes of Some Natural Glasses", Proceedings of the International Conference on Glass in Planetary and Geological Phenomena, J. Non-Cryst. Solids, 67, 169-177, (1984).

I. Graduate student thesis since 1985

S. Srilomsak, "Influence of Oxygen Activity on the Lattice Parameters and Thermal Expansion of Mg and Sr-Doped LaCrO_3 ", M.S. Thesis, May 1986. (in Thailand)

R. Koc, "Structural, Sintering and Conductivity Studies of the $(\text{La,Sr})\text{Cr}_{(1-x)}\text{Mn}_x\text{O}_3$ ", M.S. Thesis, 1986. (Scientist at NREL)

C. Yu, "Redox Kinetics and Defect Structure of LaCrO_3 and SrTiO_3 ", Ph.D. Thesis, 1986.

G. Carini, "An Apparatus for the Measurement of dc Electrical Conductivity and Seebeck Coefficient of Semiconductors as a Function of High Temperature and Oxygen Partial Pressure", M.S. Thesis, 1987. (Self Employed)

L. Kuo, "Redox Behavior of LaMnO_3 ", Ph.D. Thesis, May 1987. (Scientist at Westinghouse)

C.C. Chen, "Processing Study and Film Fabrication of Superconducting Y-Ba-Cu-O Ceramics", M.S. Thesis, 1988.

J.D. Carter, "A Pushrod Type, Controlled Atmosphere Dilatometer for Thermal and Oxygen Activity Expansion Measurements", M.S. Thesis, 1989. (Postdoc Risø Denmark)

C.J. Brannon, "Thermogravimetric, Electrical Conductivity and Thermopower Studies of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ ", Ph.D. Thesis, 1989. (Engin. GE)

R. Koc, "Investigation of the $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Cr}_y)\text{O}_3$ System", Ph.D. Thesis, 1989.

G.F. Carini II, "Electrical Conductivity, Seebeck Coefficient and Defect Structure of Ca-Doped YCrO_3 ", Ph.D. Thesis, Dec. 1990. (Self Employed)

F.C. Jang, "Dispersion Behavior of Aluminum Oxide, Lanthanum Manganite and Lanthanum Chromite Powders in Liquids", Ph.D. Thesis, May 1991. (Prof. in Taiwan)

J.D. Steibel, "Sintering of 20% Calcium-Doped, 20% Sr-Doped and Undoped LaMnO_3 ", M.S. Thesis, May 1991. (Engineer at GE)

J.W. Stevenson, "Electrical and Structural Properties of Compositions in the Systems $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ", Ph.D. Thesis, December 1991. (Scientist at Battelle NW Labs)

M.J. DeBarr, "Investigations of the Conduction Mechanism in $\text{La}_{1-y}\text{Ca}_y\text{Al}_{1-x}\text{MnO}_3$ ", M. S. Thesis, December 1991. (Engineer GM)

R. Raffaele, "Investigation of Transport Anomalies in $\text{La}_{1-y}\text{Sr}_y\text{Cr}_{1-x}\text{MnO}_3$ ", Ph.D. Thesis, December 1990. (Prof. at Florida Tech.)

J. Current graduate students involved with project

S. Sehlin is a Physics Ph.D. candidate who is continuing the work on transport mechanisms in perovskites. He was supported by this program and expects to complete his thesis by May 1994.

J. Conrad is a Ceramic Engineering M.S. candidate supported by this program and is studying the $(\text{La,Ca})(\text{Cr,Al})\text{O}_3$ system. (Dec. 1993)

M. Etchemendy is a Ceramic Engineering M.S. candidate supported by UMR funds and is studying the $(\text{La,Ca})(\text{Fe,Ni})\text{O}_3$ system. (Dec. 1993) (Engineer at Westinghouse)

D.B. Bookout is a Physics Ph.D. candidate supported by UMR funds is doing the modelling of the conduction processes. (Ph.D. Dec. 1993) (Inst. East Central College)

D. Marsh is a Physics Ph.D. candidate supported by UMR funds is doing modelling of the Seebeck coefficient in mixed oxides. Expects to complete Dec. 1994.

C. Leach is a Ceramic Engineering M.S. candidate who is supported by the project and is continuing the work on preparation and characterization of conducting oxides. Expects to complete his M.S. Dec. 1994.

III. Appendices

Reprints available on request.