

Progress Report for Time Period

Oct 1, 1990 - June 30, 1992

**Electronic Transport and Mixed Conductivity
in Perovskite Type Oxides**

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March 3, 1992

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ABSTRACT

The goal of the investigation presented in this report is to study the inter-relationship between electrical conductivity, oxidation-reduction kinetics, defect structure, and composition of n- and p-type binary and ternary transition metal oxides. The experimental part of the investigation included specimen preparation, thermogravimetric measurements, X-ray diffraction, thermally stimulated current, DTA/TGA, optical absorption, transmission electron microscopy, electrical conductivity, and Seebeck measurements. The systems studied or being studied are LaMnO_3 - LaCrO_3 - LaCoO_3 , $(\text{La,Ca})(\text{Mn,Al})\text{O}_3$, $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$, YMnO_3 - CaMnO_3 , and LaMnO_3 - CaMnO_3 . Results show:

1. that the anomalous behavior of the electrical conductivity observed in the $\text{La}(\text{Cr,Mn})\text{O}_3$ system can be explained by a combination of trapping and percolation.
2. that $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ is more stable towards reduction than $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_3$;
3. that $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ conducts via the adiabatic small polaron mechanism.
4. that $\text{La}_{1-x}\text{CrO}_3$ conducts via the nonadiabatic small polaron mechanism.
5. that $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ conducts via the nonadiabatic small polaron mechanism.
6. and that LaMnO_3 , $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ appear to contain Mn^{+2} - Mn^{+4} pairs which tend to dominate the electrical conductivity
7. that the electrical conductivity of $(\text{La,Cr})(\text{Mn,Al})\text{O}_3$ can be explained by a combination of trapping and percolation
8. that $(\text{Y,Ca})\text{MnO}_3$ and $(\text{La,Ca})\text{MnO}_3$ conduct via the adiabatic small polaron mechanism
9. that the $(\text{La,Ca})(\text{Cr,Co})\text{O}_3$ system shows disproportionation of Co^{+3} similar to that observed for Mn^{+3}

HIGHLIGHTS OF PROGRAM (October 1, 1990 - June 30, 1992)

(1) The studies in the $Y_{1-x}Ca_xCrO_3$ 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) $Y_{1-x}Ca_xCrO_3$ 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 $1450^\circ C$ without degradation of stability towards reduction.
- c) The thermal expansion coefficient can be increased from 7.7 to $9.5 \times 10^{-6} C^{-1}$ by addition of 0 and 20 mol% Ca respectively.

(2) The studies on the $(La,Sr)(Mn,Cr)O_3$ system have yielded some significant results which are significantly increasing our understanding of the conduction behavior of perovskite oxides. Results are:

- a) conduction occurs via the nonadiabatic small polaron mechanism.
- b) the seebeck data suggests that $(La,Sr)MnO_3$ contains $Mn^{+2} - Mn^{+4}$ 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.

(3) The studies on the $(La,Ca)(Al,Mn)O_3$ 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 Mn^{2+} - Mn^{4+} disproportionation (pairing) through a dependence of site energy upon adjacent site occupancy.

(4) 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.

(5) The studies in the $(\text{La,Ca})(\text{Cr,Co})\text{O}_3$ system indicate that production of Co^{4+} carriers appears to be occurring as the temperature is increased. Since an average B-site valence of 3+ must exist to maintain electrical neutrality, a possible mechanism for this increase in carriers is the thermally driven disproportionation of Co^{3+} into Co^{2+} and Co^{4+} . Such a process also accounts for the near-zero high-temperature Seebeck coefficient of LaCoO_3 and the partial suppression of the Verwey mechanism with Ca doping. Thus it appears that Co in this system mimics the behavior of the Mn containing systems.

CONTRIBUTORS TO PROGRAM

1. G. Carini, Ceramic Engineering Ph.D. candidate, who was supported by this program. He studied the influence of cation stoichiometry and dopants on YCrO_3 system. He received his Ph.D. in December 1990.
2. R. Raffaele, Physics Ph.D. candidate, studied two path hopping transport in perovskite materials. He was supported by this program and received his Ph.D. in December 1990.
3. D. Carter is a Ceramic Engineering Ph.D. candidate, who developed our high temperature controlled atm. dilatometer. He is partially supported by this program and received his M.S. degree in Dec. 1989 and expects to complete his Ph.D. in August 1992.
4. J. Stevenson is a Ceramic Engineering Ph.D. candidate who is studying the $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ system. He is supported by this program and completed his Ph.D. in December 1991.
5. S. Sehlin is a Physics Ph.D. candidate who is continuing the work on transport mechanisms in perovskites. He is supported by this program and expects to complete his thesis by May 1992.
6. M. DeBarr is a Ceramic Engineering M.S. candidate who is studying conductivity in the $\text{La}(\text{Mn,Al})_3$ system. He is supported by other funds and will complete his thesis by December 1991.
7. F. C. Jang is a Ceramic Engineering Ph.D. candidate who is studying the dispersion characteristics of 0.1 to 0.5 μm perovskite powders. He is supported by other funding and completed his thesis May 1991.

OTHER CONTRIBUTORS TO PROGRAM

1. Dr. H.U. Anderson, Curators' Professor of Ceramic Engineering and Senior Investigator, Materials Research Center, Principal Investigator and Program Director.
2. Dr. D.M. Sparlin, Professor of Physics and Co-investigator. His responsibilities are to perform the low temperature measurements on superconducting oxides, to supervise the DLTS program, and to assist with the electrical conductivity and Seebeck measurements. His years of experience in instrumentation are applied to the design of equipment and experiments for the general program.
3. Dr. Paul E. Parris, Assistant Professor of Physics. He is modelling the conduction mechanisms in the chromite, manganite and cobaltite systems.
4. Dr. Magdi M. Nasrallah, Research Professor of Ceramic Engineering. He is assisting with experimental details and giving guidance in interpretation of results.

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