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CHARACTERIZATION OF ELECTRICALLY
CONDUCTING OXIDES

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- Period -

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HIGHLIGHTS OF PROGRAM

(JULY 1, 1988 - DECEMBER 31, 1989)

- (1) 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.
- (2) 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 have now been transferred to SOFC programs sponsored by DOE-Morgantown Energy Technology Center and Ceramtec, Inc.
- (3) An elucidation of the structure of the high temperature (1400°C) phases of La substituted SrTiO_3 has demonstrated our abilities 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 defect structure of this system.
- (4) 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.
- (5) The construction of dual high temperature controlled atmosphere dilatometer has been completed. The apparatus is now being used to study the expansion and contraction that occurs in perovskite oxides as oxygen is absorbed or evolved.
- (6) An effective-medium theory of hopping transport in binary systems is explaining the conductivity changes that occur when Mn is substituted into LaCrO_3 . It appears that this theory will also apply to the LaCrO_3 - LaCoO_3 system.

WORK IN PROGRESS

The stability of the $Y_{1-x}Ca_xCrO_3$ has caused us to expand our work in the $YCrO_3$ - $YMnO_3$ - $YCoO_3$ system. The success of the use of effective medium theory to explain the conduction in $La(Cr,Mn)O_3$ is encouraging us to apply the theory to other systems (such as $(La,Ca)(Cr,Co)O_3$ and $Y(Cr,Mn)O_3$ which behave similarly.

The models that we have proposed to explain the redox behavior of $LaCrO_3$, $LaMnO_3$, $YCrO_3$, $BaTiO_3$ and $SrTiO_3$ have oxygen activity and temperature regimes in them where ionic compensation becomes important in the electrical neutrality conditions. In these regions we expect to see considerable ionic transport. In an effort to confirm this we are doing experiments with which we are measuring the ionic transport number by galvanic cell techniques. Our early data suggests that mixed conductivity is occurring in these critical regions. Such information is becoming very important for catalysis, solid oxide fuel cell electrode and oxygen pump applications. We are therefore expanding this work with the intent of defining the regions of mixed conductivity.

MANUSCRIPTS PUBLISHED OR ACCEPTED FOR PUBLICATION

- R. Koc, H. U. Anderson and S. A. Howard, "Structural, Sintering and Electrical Properties of the Perovskite $(\text{La,Sr})(\text{Cr,Mn})\text{O}_3$ ", 1st International Symposium, Elec. Chem. Soc.
- H. U. Anderson, J. H. Kuo and D. M. Sparlin, "Review of Defect Chemistry of LaMnO_3 and LaCrO_3 ", 1st International Symposium, Elec. Chem. Soc.
- S. Srilomsak, D. P. Schilling and H. U. Anderson, "Thermal Expansion Studies on Cathode and Interconnect Oxides", 1st International Symposium, Elec. Chem. Soc.
- J. H. Kuo, H. U. Anderson and D. M. Sparlin, "Oxidation-Reduction Behavior of Undoped and Sr-Doped LaMnO_3 Nonstoichiometry and Defect Structure", J. of Solid State Chem., 83, pp. 52-60 (1989).
- 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).
- 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. of Appl. Phys., Vol. 65, No. (4), pp. 1492-1498, Feb. 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).
- C. C. Chen and H. U. Anderson, "Synthesis of $\text{YbA}_2\text{Cu}_3\text{O}_{7-x}$ Superconductor by the Ethylene Diamine Process", Industry-University Advanced Materials Conference II, Denver, CO, March 6-9, 1989.

Theses

- C. J. Brannon, "An Investigation of the Low Voltage Failure Mechanism in Multilayer Ceramic Capacitors", M.S. Thesis, 1986.
- 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.
- 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.

MANUSCRIPTS PRESENTED, IN PREPARATION OR SUBMITTED

- M. J. Pennell and H. U. Anderson, "Synthesis of Oxides Via an Ethylene Glycol Process", Am. Chem. Soc., Los Angeles, CA, Sept. 28, 1988.
- H. U. Anderson, "Oxides for Fuel Cell Electrodes", Allied-Signal, Garrett Division, Los Angeles, CA, Sept. 28, 1988.
- R. Koc and H. U. Anderson, "Structural, Sintering, and Electrical Properties of The Perovskite-Type $(\text{La,Sr})(\text{Cr,Mu})\text{O}_3$ ", 41st Pacific Coast Meeting, Am. Cer. Soc., San Francisco, CA, Oct. 25, 1988.
- H. U. Anderson and D. M. Sparlin, "The Stability of LaMnO_3 Under Fuel Cell Environments", *ibid.*
- H. U. Anderson and M. J. Pennell, "Polymeric Synthesis of LaMnO_3 and LaCrO_3 ", *ibid.*
- C. C. Chen and H. U. Anderson, "The Synthesis of $\text{YBa}_2\text{CuO}_{7-x}$ Superconductor by the Ethylene Diamine Process", Industry-University Advanced Materials Conference, March 6-9, 1989, Denver, CO.
- H. U. Anderson, "Fuel Cell Cathode and Interconnect Research at UMR", EPRI Solid Oxides Electrochemistry Workshop, Palo Alto, CA, Jan. 13, 1989.
- R. Raffaele, H. U. Anderson, D. M. Sparlin and P. Parris, "Conduction Mechanism in the $\text{La}(\text{Cr,Mn})\text{O}_3$ Series", Am. Cer. Soc., Dallas, TX, April 1990.
- R. Koc, H. U. Anderson and M. M. Nasrallah, "Effect of Processing and Dopants on Air Sinterable LaCrO_3 ", *ibid.*
- R. Koc and H. U. Anderson, "Low Temperature Sintering of YCrO_3 and LaCrO_3 Based Ceramics", Ceramic Powder Processing Science, San Diego, CA, Feb. 1990.
- H. U. Anderson, C. C. Chen and J. C. Wang, "Synthesis of Conducting Oxide Films and Powders from Polymer Precursors, *ibid.*
- S. Seward, G. Carini and H. U. Anderson, "Structural, Sintering and Electrical Properties of the $\text{YCrO}_3\text{-YMnO}_3\text{-YCoO}_3$ System", 1st International Symposium on Solid Oxide Fuel Cells, El. Chem. Soc., Hollywood, FL, Oct. 1989.
- R. Koc and H. U. Anderson, "An Sinterable LaCrO_3 Based Ceramics", *ibid.*
- 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", Sub. J. Solid State Chem.
- M. M. Nasrallah and H. U. Anderson, "Acceptor/Donor Compensation in Rutile", Solid State Comm.

CURRENT AND PENDING SUPPORT

Harlan U. Anderson

Current Support

Department of Energy - BES

"Characterization of the Redox Behavior and Stability of Electrically Conducting Oxides", \$140,000

7/1/88 - 6/30/89

DOE-METC

"Development of Improved Cathodes for Solid Oxide Fuel Cells", \$162,788

2/1/89 - 1/31/90

Pending

DOE - Equipment Proposal

"Acquisition of An Analytical Transmission Electron Microscope", \$290,590

6/1/90

NSF

"Role of Polymer Precursors and Improved Reliability of Electronic Ceramics,
\$451,199

6/1/90 3 Years

Don Sparlin

Current Support

DOE - BES, (See Anderson)

CONTRIBUTORS TO PROGRAM

Students:

1. Mr. R. Koc, Ceramic Engineering is a Ph.D. candidate studying the structural and sintering characteristics of the LaCrO_3 - LaMnO_3 - LaCoO_3 system. He is supported by University funding. He completed his Ph.D. in December 1989.
2. Mr. G. Carini, Ceramic Engineering Ph.D. candidate, who is supported by this program. He is investigating the influence of cation stoichiometry and dopants on the YCrO_3 - YMnO_3 system. He will receive his Ph.D. in May 1990.
3. Mr. C. J. Brannon, Ceramic Engineering Ph.D. worked on the super conducting oxides. He completed his Ph.D. in May 1989 and is now employed by General Electric.
4. Mr. R. Raffaele, Physics Ph.D. candidate, who is studying the conductivity of perovskite materials using effective medium theory. He is supported by this program and should complete his thesis by May 1990.
5. Mr. J. D. Carter is a Ceramic Engineering M.S. candidate who is developing our high temperature controlled atm. dilatometer. He is supported by this program and received his M.S. degree in December 1989.

OTHER CONTRIBUTORS TO PROGRAM

1. Dr. H. U. Anderson, Curator's Professor of Ceramic Engineering and Senior Investigator, Materials Research Center, Principal Investigator and Program Director.
2. Dr. D. M. Sparlin, Professor of Physics, 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. J. Guha, Research Professor of Ceramic Engineering. His responsibilities are to supervise and to assist in the preparation and characterization of samples. In addition, he provides considerable experience and guidance in the interpretation of phase equilibrium diagrams.

4. Dr. P. E. Parris, Assistant Professor of Physics. He is modeling the conduction mechanisms in the chromite, manganite and cobaltite systems.
5. Dr. M. M. Nasrallah, Professor of Materials Science and Engineering at Cairo University in Cairo, Egypt, returned to our research group as a visiting professor in July 1989. He is assisting with experimental details and giving guidance in interpretation of results.

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