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SOFC MATERIALS DEVELOPMENT: CHROMITE INTERCONNECTIONS

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SOFC Materials Development: Chromite Interconnections

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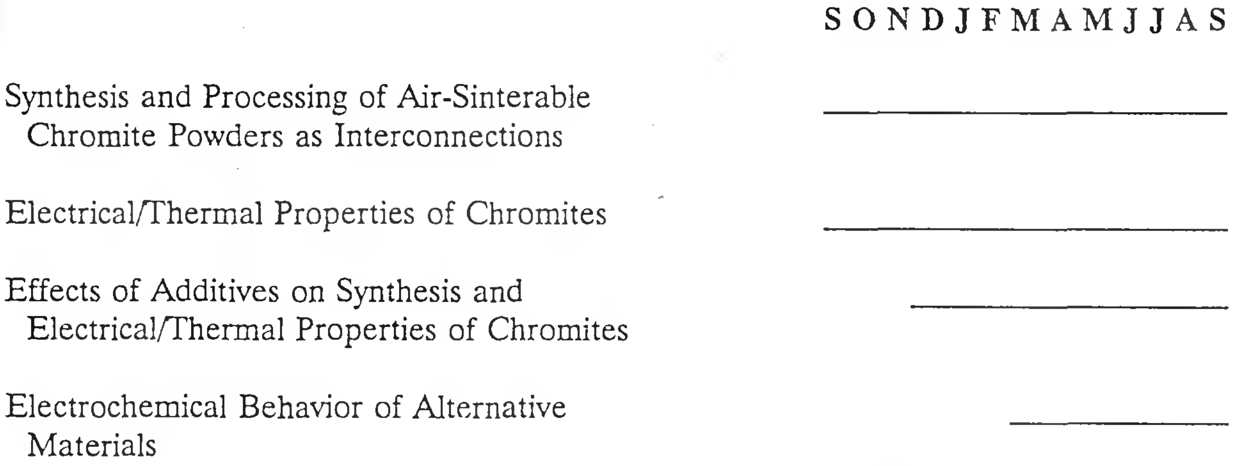

OBJECTIVES

The objectives of this research are to:

- Develop a broader selection of alternative SOFC current interconnections and air electrode materials with improved electrical, thermal and electrochemical properties leading to enhanced and long-term performance of SOFCs.
- Develop advanced synthesis and fabrication processes for both state-of-the-art $La(Sr)CrO_3$ and new and alternative materials for use as interconnection and air electrode materials in SOFCs. The materials are to be reproducibly and economically consolidated in air with the electrolyte and/or electrodes into a SOFC below 1823 K with a minimum of fabrication steps and at a low cost.

BACKGROUND INFORMATION

Solid oxide fuel cells are emerging as an attractive, clean, and efficient technology for the direct conversion of hydrogen and fossil fuels to electrical energy. The major challenge in developing SOFCs is to develop materials with acceptable electrical, thermal and electrochemical properties that can be synthesized, processed and fabricated as a high-performance fuel cell at low cost (Bates 1989).

Presently, three design concepts represent state-of-the-art SOFC: tubular, monolithic and planar. The most advanced of the three is the tubular concept. All of the state-of-the-art concepts use the same general materials as electrolyte, air electrode, fuel electrode, and interconnection. The air electrode is $La(Sr)MnO_3$ (sometimes containing ZrO_2); the electrolyte is Y_2O_3-stabilized ZrO_2; the fuel electrode is a ZrO_2/Ni composite; and the current interconnection is either $La(Mg)CrO_3$ or $La(Sr)CrO_3$. Although these same materials are generally used in the state-of-the-art tubular, monolith and planar SOFC, each cell design is generally fabricated by a different processing method, although some common processes are being considered.

The use of these different chromite, manganite, zirconia and nickel material combinations potentially results in several fabrication and performance-related limitations. The most critical problems are the thermal expansion mismatch between these materials, the low electrical conductivities (primarily of the air electrode) and the complex fuel cell fabrication/process steps required. Critical thermal, electrochemical and electrical properties are compromised in order to achieve compatibility between materials and improved fuel cell performance.

An important issue and key to the development of a low-cost, high-performance SOFC is the ability to sinter the $La(Sr)CrO_3$ interconnection in air at temperatures between 1723 and 1823 K. The $La(Sr)MnO_3$ now used as the air electrode is unstable at low oxygen partial pressures. Reduction of the manganites results in structural, property and composition changes, all of which cannot be recovered by reoxidation. Therefore, the $La(Sr)MnO_3$ must be fabricated in high-oxygen partial pressures, such as air. In contrast, the $La(Sr)CrO_3$ used as the interconnection sinters to high density with closed porosity better in highly reducing conditions than in air. However, because the $La(Sr)CrO_3$ is stable in both oxidizing and reducing conditions, significant benefits in SOFC fabrication and costs could be realized if the $La(Sr)CrO_3$

could be sintered in air below 1823 K to high density with totally closed porosity.

The accepted "Pechini" process for chromite synthesis does not presently produce powders that can be sintered in air without additives at 1823 K. Sintering in air at 1823 K results in low densities between 60 and 85% of the theoretical density with open porosity. Recently, a new Glycine-Nitrate process has been developed that can synthesize highly active La(Sr)CrO_3 powders which sinter to high density with closed porosity in air at or below 1823 K.

The availability of highly active $La_{1-x}Sr_xCrO_3$ powders that can be sintered at 1823 K has enabled identification of previously unknown factors that affect air sintering of the chromite, and opened avenues for studying the air-sintering mechanism(s). In addition, the role(s) of these factors on the $La_{1-x}Sr_xCrO_3$ properties can be assessed. Through an understanding of the factors affecting air sintering, synthesis processes might be altered to increase sintered densities; reduce the open porosity; improve the electrical, thermal and structural properties; lower the air sintering temperature and synthesize powder for the low-cost fabrication processes for all SOFC concepts.

PROJECT DESCRIPTION

This research and development project is an effort to modify state-of-the-art SOFC materials or develop analogous SOFC materials as electrodes and interconnections that will provide improved electrical, thermal expansion and electrochemical properties. This work includes four tasks:

- **Material Synthesis and Processing Technology** is being developed to modify state-of-the-art and alternative interconnection materials (powders) that can be sintered in air below 1823 K with and without the use of metal additives as sintering aids.

- **Additive Effects** on structure, synthesis and electrical and thermal properties are being studied for interconnection materials based on $La_{1-x}Sr_xCr_{1-y}Al_yO_3$.

- **Electrical and Thermal Properties** of alternative interconnection materials are being evaluated as functions of composition, structure and synthesis/fabrication methods.

- **Electrochemical Behavior** of materials and SOFC interfaces is being studied using complex AC impedance techniques coupled with simple cell geometries.

The content of this report discusses R&D directed toward determining the factors that affect the air sinterability of $La_{1-x}Sr_xCrO_3$.

RESULTS

Synthesis of $La_{1-x}Sr_xCrO_3$

A new route to the synthesis of high-quality, homogeneous, ultra-fine crystalline ceramic powders from an aqueous solution has been developed. This "Glycine-Nitrate" process(a) developed at Pacific Northwest

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(a) Applications for U.S. and foreign patents have been filed for the United State Government and Battelle Memorial Institute.

Laboratory has been reported previously. (See Bates, Chick and Weber 1989; and Chick et al. 1989). Briefly, the "Glycine-Nitrate" process utilizes an aqueous solution of La, Sr and Cr nitrates and a low molecular amino acid, glycine. The glycine enhances the solubility of the metal cations, complexing them either through the amine or carboxylic acid ends of the molecule. The solution is then heated until most of the water has evaporated. The remaining viscous liquid contains the metal ions complexed by the glycine. At a few hundred degrees Celsius, the viscous liquid ignites, producing an ash. The ash is calcined and sonicated before being pressed and sintered in air.

The $La_{1-x}Sr_xCrO_3$ powders synthesized by the Glycine-Nitrate process are single-phase perovskite crystallites with a single composition. The crystallites vary in size from 6 to 60 nm in size, but generally vary from 20 to 40 nm. The powders have surface area up to 32 m^2/g. The particles form only soft agglomerates that are easily broken by sonication without milling. These powders, when certain factors are met, can be cold pressed and sintered in air at 1823 K to greater than 96% TD with total closed porosity.

Air Sintering of $La_{1-x}Sr_xCrO_3$

The availability of the highly active $La_{1-x}Sr_xCrO_3$ powders enables previously unknown or at least unreported factors influencing air sintering of $La_{1-x}Sr_xCrO_3$ to be identified and opens avenues to study sintering mechanism(s). The gross effects of temperature, chromium vaporization and atmosphere (oxygen pressure) were easily recognized previously using the significantly less active powders synthesized by the "Pechini" method. However, the role(s) of these factors has been further elucidated using the highly reactive Glycine-Nitrate synthesized powders.

Several important factors that influence air sintering of $La_{1-x}Sr_xCrO_3$ are recognized in this study:

- powder morphology
- temperature
- sintering atmosphere
- cation ratios
- vapor loss
- additives and contamination
- second phases and particle composition.

Many of these factors are synergistic, such as cation ratio/vapor loss/second phases.

The effects of powder morphology, temperature and sintering atmosphere on $La_{1-x}Sr_xCrO_3$ sintering are major, recognized factors and are only briefly summarized. Although the volatilization of chromites has been measured, its effect on sintering has not been resolved. The roles of cation ratio, additives/contamination and second phase and particle composition have not been recognized before and will be discussed in more detail.

Powder Morphology. The ability to sinter $La_{1-x}Sr_xCrO_3$, like most ceramic powders, is highly dependent upon the morphology of the powder. Uniform, submicrometer particles, high surface area, uniform composition and structure and the absence of hard agglomerates all enhance the sinterability in air and lower sintering temperatures. It is these same factors that make the $La_{1-x}Sr_xCrO_3$ powders synthesized by the Glycine-Nitrate process amenable to air sintering.

Temperature. Increased sintering temperatures generally result in increased sintering rates and higher densities. However, for $La_{1-x}Sr_xCrO_3$, increasing the temperatures above approximately 1750 K results in high, incongruent vaporization with Cr loss, which influences the sintering process.

Atmosphere. It has generally been recognized that sintering in highly reducing atmospheres, $\approx 10^{-10}$ atmospheres of oxygen, increases the sinterability of $La_{1-x}Sr_xCrO_3$. The actual reason for this enhancement is not fully known, but thought to be related to Cr vapor loss. No attempt has yet been made to sinter the $La_{1-x}Sr_xCrO_3$ powder of this study in reducing atmospheres.

The chromites are also susceptible to oxygen reduction and defect formation (Flandermeyer et al. 1984; Anderson, Kuo and Sparlin 1989.)

Cation Ratios. The sinterability of $La_{1-x}Sr_xCrO_3$ in air at 1823 K varies significantly with relatively small changes in composition, particularly with (Ca+Sr)/Cr and La/Sr ratios. These effects are highly synergistic with the other effects. A series of $La_{1-x}Sr_xCrO_3$ powder compositions were synthesized by the Glycine Nitrate process. The $La_{1-x}Sr_xCrO_3$ powders were calcined at 923 K in air for one-half hour, sonicated, uniaxially pressed and then isostatically pressed at 145 MPa before sintering in air at 1823 K for 8 h.(a)

The compositions of the $La_{1-x}Sr_xCrO_3$ are plotted in Figure 1. The lettered compositions (A-B and C-D) represent variations in cation ratios and compositions where sintering densities and weight changes are compared. The six-sided, dashed line figure is discussed in a later section.

The sintered density increases markedly with increasing Sr content for compositions that have (La+Sr)/Cr=1.00 (Figure 2). These compositions represent line A-B in Figure 1.

Both moderate additions and depletions of Cr enhance the sintering of $La_{1-x}Sr_xCrO_3$ in stagnant air as shown by the solid line in Figure 3. These compositions refer to line C-D in Figure 1. At 24% Sr substitution, a maximum sintered density (95% of theoretical) is obtained at (La+Sr)/Cr=1.04. However, the sintered $La_{1-x}Sr_xCrO_3$ samples that are depleted in Cr contain a second phase of La_2O_3, which hydrolyzes in the presence of water vapor, resulting in the fracturing of the material. The minimum in sintered density observed at the stoichiometric composition of (La+Sr)/Cr=1.00 is not understood.

Vapor Loss. As discussed above, at high temperatures, cations in the $La_{1-x}Sr_xCrO_3$ vaporize, resulting in composition changes and changes in sinterability. Cr appears to be the major cation that vaporizes. By surrounding the green $La_{1-x}Sr_xCrO_3$ with $La(Sr)CrO_3$ during sintering, Cr loss is reduced; some compositions become denser, while others decrease in density. Anderson, Kuo and Sparlin (1989) indicate that vapor loss can be significant above 1275 K and is a function of oxygen partial pressure, water content, sintering atmosphere and cation addition levels.

(a) The fabrication technique used for these pellets does not represent optimum sintering conditions necessary for highest densities, but is designed to reveal relative effects quickly.

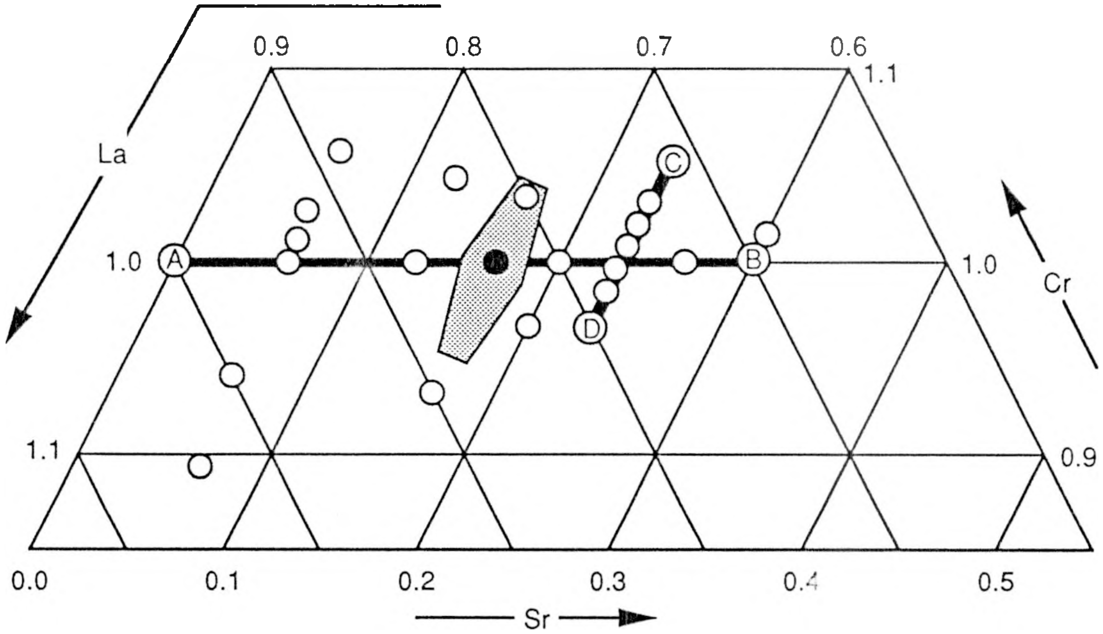

Figure 1. Ternary $La_{1-x}Sr_xCrO_3$ Compositions. Numbers refer to formulation: $La_wSrxCr_yO_3$ where w+x+y = 2.0

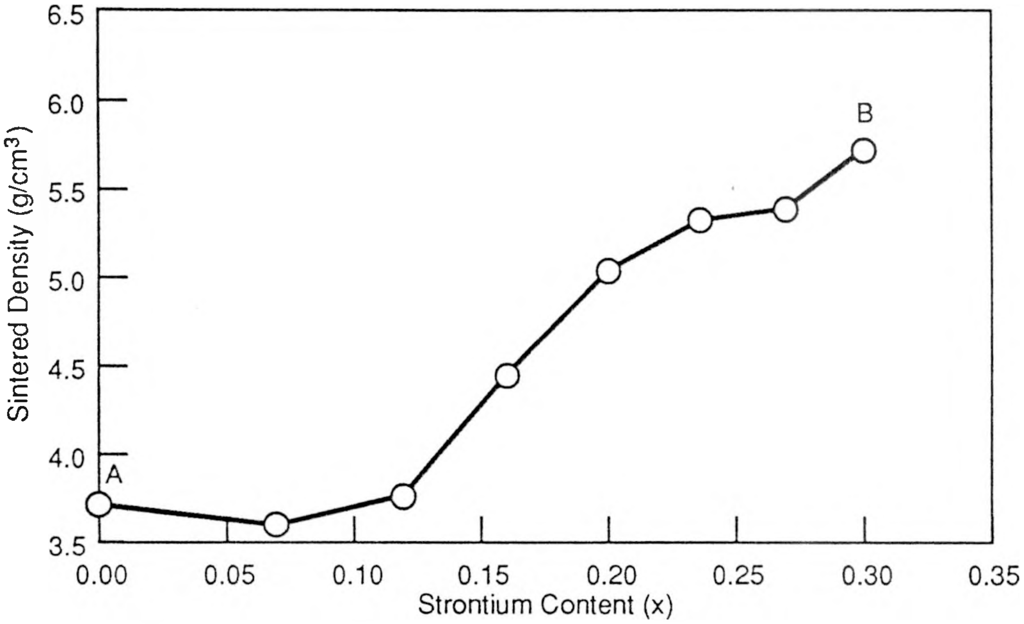

Figure 2. Sintered Density As Function Sr Content With (La+Sr)/Cr = 1.00. Compositions represent line A-B, Figure 1

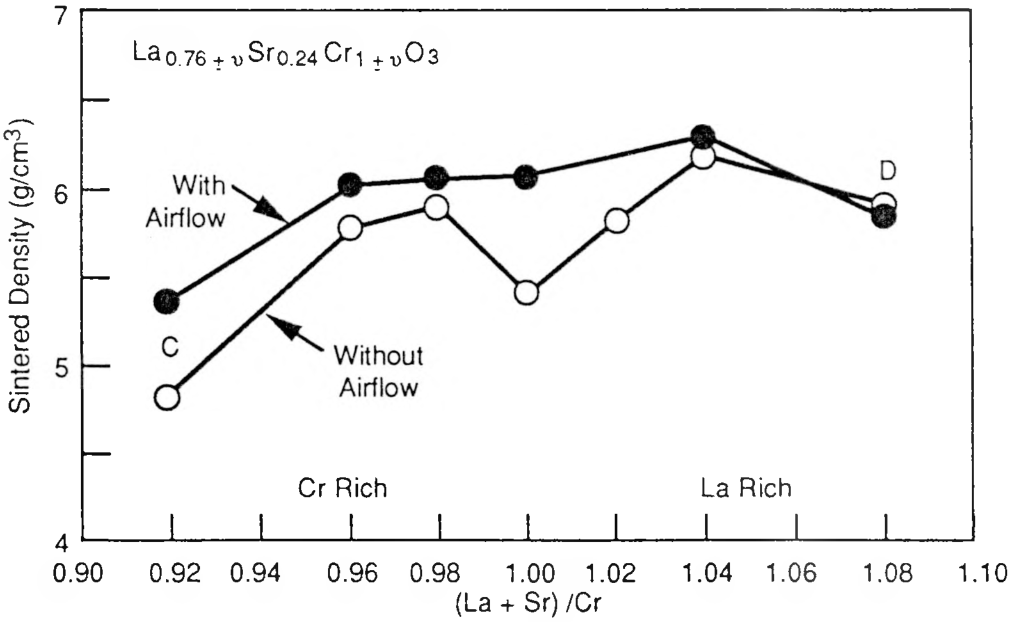

Figure 3. Sintered Density as Function of (La+Sr)/Cr Ratio For $La_{0.76-y}Sr_{0.24}Cr_{1.00+y}O_3$. Compositions represent line C-D in Figure 1

The air sinterability and sintered densities of $La_{1-x}Sr_xCrO_3$ with (La+Sr)/Cr <1.04 can be improved by increasing air flow across the $La_{1-x}Sr_xCrO_3$ during sintering. Samples of $La_{1-x}Sr_xCrO_3$ along the solid composition line C-D in Figure 1 were sintered in a resistance-heated furnace chamber with an approximately 3-liter volume of relatively "dead" air. Sintering under increased air flow was accomplished by inserting an air inlet tube into the top of the furnace and an outlet tube through the bottom. Approximately 4.7 l/min (10 SCFH) of room air was passed through the furnace during sintering. The sintered densities achieved in flowing air are shown in Figure 3. The Cr-rich compositions show higher densities in flowing air, but the Cr-depleted compositions showed little or no change. The largest effect on sintered density was for (La+Sr)/Cr = 1.00, where the "valley" in stagnant air was essentially removed by increasing the air flow.

The weight losses, corrected for water loss,(a) were higher in flowing air than in stagnant air. This loss is attributed to increased volatilization of chromium and, perhaps, other oxide species. The weight loss decreases with increasing Cr depletion (Figure 4). Anderson et al. (1977) indicate that the substitution of Sr into $LaCrO_3$ does not influence its volatility in 10^{-3} atm of O_2. However, we have found that weight loss during sintering increases with Sr additions along A-B (Figure 1).

(a) Other experiments show that approximately 0.8% of the total weight loss during sintering is due to loss of adsorbed water.

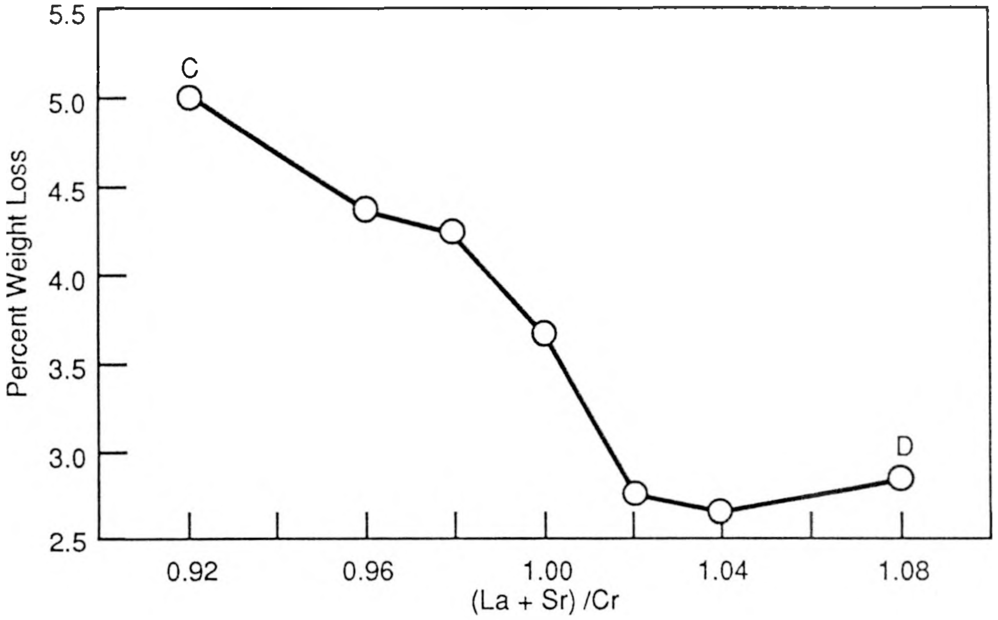

Figure 4. Weight Loss During Sintering in Stagnant Air as Function of (La+Sr)/Cr, Corrected for 0.8 wt% Loss Adsorbed H_2O. Compositions represent line C-D in Figure 1

The actual loss of Cr or other cations during sintering is currently being determined from an analysis of the cation compositions after sintering. Therefore, we can only speculate as to the composition changes resulting from volatilization. However, assuming Cr to be the major volatile cation, it is likely that all compositions become more depleted in Cr during sintering. This could explain the higher sintered densities for compositions with (La+Sr)/Cr ≥ 1 (Figure 3). However, it is not consistent with higher sintering rates in reducing atmosphere, where Cr vaporization is reported to be lower than in air (Anderson et al. 1977). In the reported studies, the volatility of chromites in gases containing 10^{-3}atm 0_2 and 10^{-1}atm H_20 was greater than that of chromites in 10^{-3}atm 0_2 gases without water.

For the materials shown in Figure 3, the increased air flow results in increased vapor loss and further depletion of the Cr. In turn, these more Cr-depleted materials sinter to higher density.

Overall, the interrelationships between cation ratios, vaporization, furnace atmosphere and sintering rates are not well understood. Analyses of these interactions are continuing.

Additives and Contamination. The effects of alumina on $La_{1-x}Sr_xCrO_3$ sinterability appear complex. Aluminum can either enhance or inhibit the air sinterability of $La_{1-x}Sr_xCrO_3$, depending on how Al is added to the composition: 1) to the lattice, 2) as a contaminant from Al_2O_3 particles, or 3) from close association of Al_2O_3 with the sintering body. Al_2O_3 near the chromite absorbs Cr from the vapor phase during sintering; this in turn can increase the density of the chromite adjacent to the Al_2O_3. For example, when $La_{0.76}Sr_{0.24}CrO_3$ is placed on an alumina plate and covered with an alumina crucible during sintering, the sintered density is increased over that obtained when the sample is similarly surrounded by zirconia. By absorbing the Cr vapor, the Al_2O_3, unlike the zirconia, decreases the Cr vapor pressure within the crucible, subsequently enhancing Cr vapor loss from the sample. However, if the Sr substitution is reduced, or other cation ratios changed, the presence of Al can inhibit sintering.

Previous experiments showed that the surfaces of certain $La_{1-x}Sr_xCrO_3$ compositions sinter to very high densities when aluminum was substituted for a portion of the chromium (Chick et al. 1989). However these experiments were performed before we had developed the EDTA titration to control cation stoichiometry to within ±0.5%. The magnitude of property variability resulting from uncontrolled stoichiometry is discussed later. One recent experiment performed using EDTA control of the stoichiometry resulted in a reduction in the sintered density by the addition of alumina. Therefore, lacking further results with EDTA control, it can be said only that partial substitution of the Cr by Al appears to increase $La_{1-x}Sr_xCrO_3$ sinterability in some (La+Sr)/Cr composition regions and to decrease sinterability in other regions.

Second Phases. The appearance and subsequent disappearance of minor, secondary phases with increasing temperatures results in notable changes in the sintering rates of $La_{1-x}Sr_xCrO_3$. The shrinkage curves for two $La_{1-x}Sr_xCrO_3$ compositions are shown in Figure 5. Dilatometer studies of green $La_{1-x}Sr_xCrO_3$ pellets were conducted at 100 K/h. The $LaCrO_3$ displays a smoothly increasing shrinkage rate as temperature is increased suggesting a simple, single sintering mechanism process. The $La_{0.73}Sr_{0.27}CrO_3$ shows three distinct inflections in the sintering curve near 1340, 1530, and 1800 K. This suggests phase transitions (or second phase transformation) occur that influence sintering mechanisms. The large increase in sintering rate near 1530 K coincides with melting of a secondary phase containing Sr, thought to be $SrCrO_4$. $SrCrO_4$ and La_2CrO_4 had been observed previously in calcined Glycine-Nitrate synthesized powders (Chick et al. 1989).

The $La_{1-x}Sr_xCrO_3$ ash synthesized by Glycine Nitrate at flame temperatures near 1720 K is single phase. At this high temperature, Sr is dissolved within the major $La_{1-x}Sr_xCrO_3$ perovskite phase. However, at lower temperatures, Sr has only limited solubility in $La_{1-x}Sr_xCrO_3$. Therefore, after calcination of the ash at 920 K, a minor Sr-rich phase is exsoluted from the major phase. During sintering, this Sr-rich phase undergoes structural changes and then melts at near 1530 K. The extra Sr subsequently tends to re-dissolved into the perovskite phase. However, the transient liquid phase is believed to promote shrinkage resulting from liquid-phase sintering, which accounts for the large inflection in the curve near 1530 K in Figure 5.

The causes of the other two inflections are, as yet, unknown. The higher temperature inflection shifts position and magnitude with minor changes in composition. Studies of these shrinkage-rate inflections and the associated phase behavior continues.

Analytical Development

The significant effects on the sintering behavior resulting from small differences in powder compositions and the potential composition changes resulting from vapor loss during sintering have required the use of more precise analytical procedures. The analytical needs relate to the accurate determination of the compositions for both starting metal nitrate solutions used in the Glycine Nitrate process and for oxides after synthesis, calcining and sintering. Both compositions are critical in studying the air-sintering mechanism of $La_{1-x}Sr_xCrO_3$.

EDTA. The ethylenediamine tetraacetic acid (EDTA) potentiometric titration technique was developed for analyzing the metal nitrate solutions. This single technique, is used for all solutions. It has a precision, which has been standardized using ultra-pure copper metal, on the order of 0.1 to 0.4% compared with the relative errors of 4 to 5% for the inductive coupled plasma atomic emission spectroscopy (ICP) used previously.

The importance of composition control during synthesis is illustrated by the six-sided envelope shown in Figure 1. This envelope represents the composition range that might be produced when making the central composition (solid circle) using metal nitrate stock solutions analyzed with a ±5% precision.

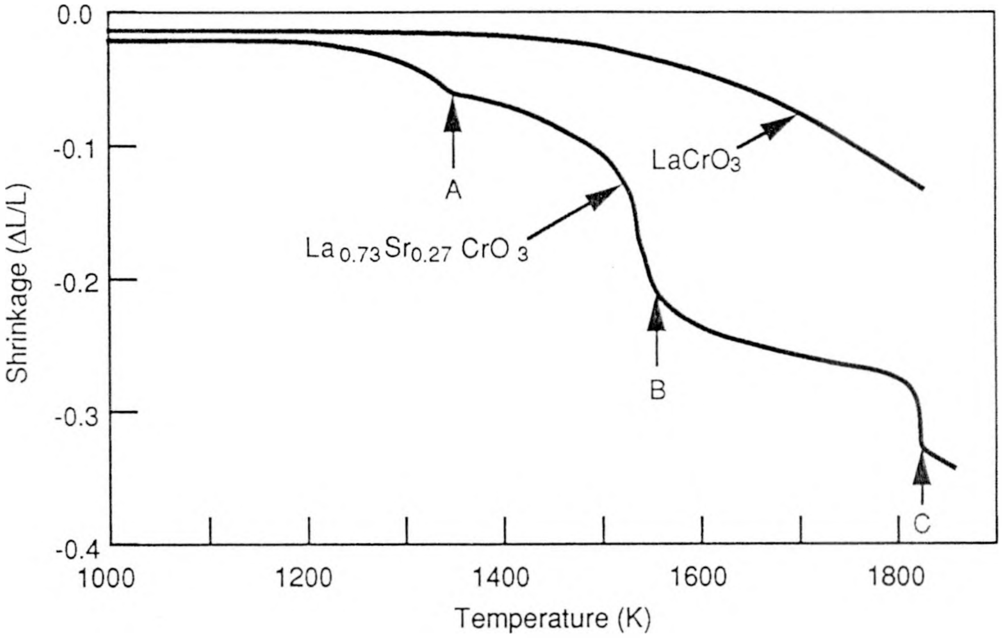

Figure 5. Sintering During Sintering at 100 K/h for $LaCrO_3$ (solid line) and $La_{0.73}Sr_{0.27}CrO_3$ (dashed line)

From top to bottom of this envelope, sintered densities in air can vary by about 50%. EDTA titration results in a composition envelope that is smaller than the center circle.

X-ray Florescence. X-ray florescence (XRF) is used to determine compositions of the $La_{1-x}Sr_xCrO_3$ powders and sintered samples. When the XRF is calibrated using oxides of known compositions, the results are precise enough to determine changes in composition due to volatilization.

CONCLUSIONS

- The synthesis of active $La_{1-x}Sr_xCrO_3$ powders that can be sintered in air at 1823 K has led to the identification of new factors in air sintering of the material, the elucidation of roles for previously known factors, the recognition of synergism between factors, and an improved understanding of the air sintering of $La_{1-x}Sr_xCrO_3$. The factors are powder morphology, temperature, sintering atmosphere, cation ratios, volatility or vapor loss, additives and contamination, and second phases. Most of these factors are synergistic.

- Three important effects not previously recognized in the air sintering of $La_{1-x}Sr_xCrO_3$ are: 1) Small variations in composition, cation ratios and second phases influence significantly the final sintered density at 1823 K, 2) Cr loss during sintering and air flow over chromite alter sintering behavior, and 3) Al additions/impurities can enhance or inhibit air sintering.

- When the factors influencing sintering are properly selected and controlled in the $La_{1-x}Sr_xCrO_3$ synthesized powders, densities greater than 95% TD with closed porosity can be achieved in air at 1823 K.

- Improved analytical methods are necessary in controlling the compositions of powders and in evaluating the factors that influence the air sintering of $La_{1-x}Sr_xCrO_3$.

FUTURE WORK

Material Synthesis and Processing

Study of the roles of vapor loss, second phases and cation ratios on the air sinterability of $La_{1-x}Sr_xCrO_3$ will continue. The effects of these factors on the thermal, electrical and electrochemical properties will be studied in an effort to increase density and reduce sintering temperatures.

The technology for synthesizing lanthanum chromites and manganites by the Glycine-Nitrate process will be transferred to U.S. industry for commercial scale-up and use.

Additive Effects

The role of Al additives on the synthesis, air sintering and properties of $La_{1-x}Sr_xCr_{1-y}Al_yO_3$ will be studied. Study will continue on the effects of air sintering aides that do not alter the $La_{1-x}Sr_xCrO_3$ composition or introduce impurities.

Electrical and Thermal Properties

The effects of composition, synthesis and fabrication, and structure on the electrical transport and thermal expansion characteristics of the chromites will be determined.

Electrochemical Processes

The electrochemical interaction studies of these alternative $La_{1-x}Sr_xCrO_3$ materials and interfaces between the SOFC electrodes will be initiated.

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