SINTERING AND PROPERTY CHARACTERIZATION OF STRONTIUM-DOPED LANTHANUM CHROMITE

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ABSTRACT

The sintering of La_{0.85}Sr_{0.15}CrO_3 (LSC-15) SOFC interconnect material can be significantly enhanced by doping with transition elements, such as Cu, Co, V and Ni, on the chromium B-site. Optimized compositions yielded densities greater than 93% theoretical after sintering at 1550°C for 2 hours, compared to <70% theoretical for un-doped stoichiometric LSC-15. Detailed XRD and DTA was used in an attempt to establish phenomena responsible for sintering, in particular the presence of low melting temperature second phases. High density materials were also evaluated for thermal expansion and electrical conductivity in air.

INTRODUCTION

Doped lanthanum chromites (LaCrO_3) have been used as solid oxide fuel cell (SOFC) interconnects for over 30 years. A primary requirement for potential interconnect materials is that they be dense enough to prevent cross leakage of fuel and oxidant gases. In recent years much consideration has been given to the sintering behavior and properties of Ca-doped LaCrO_3 (LCC), an attractive candidate because of its low sintering temperature. Detailed investigations by Chick et al. (1) established sintering mechanisms in air for non-stoichiometric La_{0.7}Ca_{x}CrO_3 (0.25≤x≤0.35), and showed that slight A-site enrichment (x=0.31) resulted in high density materials at temperatures as low as 1400°C. This phenomenon was attributed to the formation of two distinct transient liquid phases, CaCrO_4 (m.p. 1073°C) and Ca_3(CrO_4)_2 (m.p. 1253°C). Stoichiometric (x=0.30) and A-site depleted (x<0.30) samples indicated the presence of only CaCrO_4, and achieved significantly lower densities than the A-site enriched compositions. A number of recent studies, however, have indicated that LCC may not be the most suitable candidate for application as an SOFC interconnect. Armstrong et al. (2) showed that LCC materials exhibit greater isothermal expansion than Sr-doped LaCrO_3 (LSC) at SOFC operating temperatures under low oxygen partial pressures (10^{-16} atm). Paulik et al. (3) have demonstrated that the flexural strength of Ca-substituted chromites decreases with increased temperature, while Sr-doped chromites show no change in strength over a wide temperature range. The poor performance of LCC has generated renewed interest in Sr-doped LaCrO_3, though it is more difficult to sinter LSC materials to high density in air. Recent work carried out on (La_{0.7}Sr_{0.3})_xCrO_3 (4), where 0.95≤x≤1.05, has indicated similar sintering phenomena to non-stoichiometric LCC materials. A-site enriched (x>1.00) samples exhibited 2 rapid shrinkage events, giving densities of ~94% theoretical at 1650°C, due to the formation of SrCrO_4 (m.p. 1253°C) and Sr_{2.67}(CrO_4)_2 (m.p. 696°C).
Similar behavior has been observed with \((\text{La}_{0.85}\text{Sr}_{0.15})_\text{CrO}_3\) (LSC-15) for \(x \geq 1.00\) (5). As little as 1 mol% A-site excess (\(x = 1.01\)) results in closed porosity at 1650°C for 2 hours. For \(x \leq 1.00\) densities were less than 70% theoretical.

This work considers the sinterability of B-site doped LSC-15 of the general formula \(\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{1-x}\text{M}_{x}\text{O}_3\), where M denotes a transition metal and \(y\) is typically 0.02-0.10. In addition, the sintering behavior of non-stoichiometric compositions \((\text{La}_{0.85}\text{Sr}_{0.15})_\text{Cr}_{1-x}\text{M}_{x}\text{O}_3\) (0.95 \(\leq x \leq 1.05\) and 0.02 \(\leq y \leq 0.10\)) have also been investigated. A number of studies have considered the effects of transition metal dopants, such as Fe (6), Ni (7) and Co (7-8), on conductivity, thermal expansion and LaCrO\(_3\) phase stability, though few have investigated their effects on chromite sintering. Recently, however, Larsen et al. (9) reported high densities (>95% theoretical at 1520°C-2hours) for LaCrO\(_3\) co-doped on the B-site with Mg and V. The high sinterability of these materials was believed to be associated with the formation of liquid phases though exact mechanisms responsible were not determined. Prior investigations by Hayashi et al. (10) showed that Cu and Zn B-site dopants also aided sintering. Compositions \(\text{LaCr}_{0.95}\text{Cu}_{0.05}\text{O}_3\), \(\text{LaCr}_{0.9}\text{Zn}_{0.1}\text{O}_3\) and \(\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{Zn}_{0.05}\text{O}_3\) could be sintered close to theoretical density at 1600°C.

In addition to high density, interconnect materials must satisfy a number of other property requirements, including thermal expansion matching to other SOFC components and good electrical conductivity. Thermal expansion behavior and electrical conductivity in air were assessed for high density samples produced in this study. Thermal expansion matching between fuel cell components is paramount due to the thermal cycling of the device between room temperature and 1000°C. The thermal expansion coefficient (TEC) of the 8-YSZ electrolyte is typically \(10.5 \times 10^{-6}°\text{C}^{-1}\) (RT to 1000°C). Recent work by Hiei et al. (11) studied TEC control of \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{M}_{x}\text{O}_3\) (0.05 \(\leq x \leq 0.10\)) by transition metal (denoted by M) doping. TEC of the undoped material was recorded as \(9.6 \times 10^{-6}°\text{C}^{-1}\) in air, but could be increased to more closely match the electrolyte thermal expansion by co-doping with 2 mol% Co and 2 mol% Al.

With respect to electrical conductivity, undoped LaCrO\(_3\) is a p-type conductor and exhibits low electronic conduction at 1000°C in air (0.6-1.0 S/cm) (12). However, at high \(p\text{O}_2\), doping of lanthanum chromite by substituting lower valency cations on A or B lattice sites results in a charge compensation (Cr\(^{3+}\) to Cr\(^{4+}\)) transition and subsequent enhancement in the electronic conductivity. This study considers variations in electrical conductivity using 15 mol% Sr\(^{2+}\) acceptor dopant on the A-site together with either acceptor or donor substitutions on the B-site.

**EXPERIMENTAL**

Powders of the chemical formula \(\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{1-x}\text{M}_{x}\text{O}_3\), where M = Al, Co, Cu, Fe, Mg, Ni and V and 0.02 \(\leq y \leq 0.10\), were synthesized by the glycine-nitrate process using a stoichiometric fuel/oxidant ratio (13). These compositions will subsequently be referred to as LSCCu-1505, denoting 15 mol% Sr substitution for La on the A-site and 5 mol% Cu substitution for Cr on the B-site, LSCNi-1510 denoting 15 mol% Sr substitution for La on the A-site and 10 mol% Ni substitution for Cr on the B-site, etc. Powder used for sintering shrinkage measurements was calcined at 650°C for 30 min to remove residual carbon, and uniaxially pressed into bars (20 mm x 10 mm x 5 mm) at 33 MPa and then...
isostatically at 130 MPa. Sintering shrinkage tests were carried out in a Unitherm Model 1161 vertical pushrod dilatometer with a 40 g load from room temperature to 1600°C at a heating rate of 2°C/min.

Density-temperature relationships were investigated from 1250°C to 1650°C. At each designated temperature, four samples of each composition were sintered for 2 hours, and their densities measured by the Archimedes' method using ethyl alcohol. Relative densities were calculated as a percentage of the theoretical density for each doped LSC-15 composition, which had been established through x-ray diffraction (XRD) and subsequent unit cell refinement.

XRD analysis was carried out on calcined powders, and on pressed samples air-quenched after heating to relevant temperatures for each composition. Quenched samples were crushed, ground and screened through a 200-mesh sieve prior to analysis. X-ray data was recorded between 15° and 80° 2θ with 0.05° steps, and a 2 sec count using a Philips Wide-Range Vertical Goniometer and a Philips XRG3100 X-ray Generator. Semi-quantitative XRD phase analysis was used to establish weight proportions of detected non-perovskite phases.

Differential thermal analysis (DTA) of the LSC-15 compositions was conducted using a Netzsch Model 409 DTA. Samples were analyzed from room temperature to 1500°C with a heating rate of 5°C/min. XRD and DTA was also conducted on prepared powder mixtures of SrCrO₄ (a principle non-perovskite phase detected by XRD), and oxides of various B-site dopants to determine possible interactions between these components.

Thermal expansion behavior was analyzed from room temperature to 1200°C at a heating rate of 2°C/min using the aforementioned dilatometer. Electrical conductivity of sintered bars (nominal dimensions: 30 x 3 x 3 mm) was measured as a function of temperature (200 to 1000°C) in air by a four-point dc method using platinum electrodes.

RESULTS AND DISCUSSION

Sintered Density and Sintering Shrinkage Analysis

Table 1 shows densities for B-site doped LSC-15 samples after sintering at 1550°C for 2 hours. Compositions with densities ≥ 93% theoretical were subjected to more extensive investigation. Figure 1 shows the relationship between density and sintering temperature for LSC-15 compositions containing 5 mol% Co, 5 Cu, 2 Cu, 10 Ni and 5 V. At 1550°C all five compositions attain equivalent densities (93-96% TD). At lower temperatures, 1450 and 1350°C, only the Cu-doped materials achieve densities > 90% theoretical. 2 mol% Cu substitution for Cr is sufficient to significantly enhance the densification of LSC-15.

Figure 2 illustrates the shrinkage behavior of the B-site doped LSC materials compared to the base material LSC-15. Only Cu-doped samples indicate very rapid shrinkage (around 1050°C), which can almost certainly be attributed to particle rearrangement during the initial stages of liquid phase sintering. All other compositions

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show increases in the rate of densification around 1150-1200°C, but shrinkage occurs gradually over a 200-300°C temperature range. This type of shrinkage is more indicative of a solution-reprecipitation process. The non-existence of particle rearrangement might indicate insufficient liquid to coat the grains and promote rapid densification.

Table I. Densities of various La$_{0.85}$Sr$_{0.15}$Cr$_{1-x}$M$_x$O$_3$ compositions after sintering at 1550°C for 2 hours.

| Mol% B-Site Dopant in LSC-15 | % Theoretical Density (1550°C - 2h) | Mol% B-Site Dopant in LSC-15 | % Theoretical Density (1550°C - 2h) |
|-----------------------------|------------------------------------|-----------------------------|------------------------------------|
| LSC-15                      | 71.8                               | 10 Al                       | 62.5                               |
| 5 Al                        | 75.1                               | 5 Fe                        | 70.1                               |
| 10 Co                       | 95.3                               | 5 Mg                        | 85.2                               |
| 5 Cu                        | 95.3                               | 10 Mg                       | 90.1                               |
| 5 Ni                        | 82.9                               | 5 Ni                        | 82.9                               |
| 2 Cu                        | 96.3                               | 5 V                         | 94.6                               |

Previous work on La$_{0.7}$Sr$_{0.3}$CrO$_3$ (LSC-30) (4) has shown that the melting of second phases, in particular SrCrO$_4$ (m.p. 1253°C), which exsolves from the perovskite due to poor solid solubility at lower temperatures, play a major role in liquid sintering. SrCrO$_4$ is also present in smaller quantities in calcined La$_{0.85}$Sr$_{0.15}$CrO$_3$ (LSC-15) (5), though the amount is thought to be insufficient to act as an effective liquid sintering aid. XRD data for 5 mol % Co, 5 Cu, 10 Ni and 5 V doped compositions and the base material LSC-15, calcined for 1 hour at 1000°C, are shown in Figure 3. For samples containing Co, Cu and Ni, the only non-perovskite phase detected is SrCrO$_4$, observed in similar amounts (typically 1-3 wt%) in undoped LSC-15. However, LSCV-1505 (5 mol% V) reveals the presence of Sr$_3$(VO$_4$)$_2$ (~3 wt%) with no detectable SrCrO$_4$. Sr$_3$(VO$_4$)$_2$ has been observed by other workers (9) studying the effects of Mg and V double B-site doped lanthanum chromites. According to the SrO-V$_2$O$_5$ phase diagram (14), Sr$_3$(VO$_4$)$_2$ melts at 1545°C, and hence the melting of this phase does not explain the shrinkage observed around 1150°C in LSCV-1505. Equally, the presence of SrCrO$_4$ in Cu, Co and Ni doped samples does not account for the enhanced densification of these materials, since it occurs in similar amounts in poorly sintered LSC-15.

To further investigate the presence of non-perovskite phases, each composition was heated to the onset of enhanced sintering (determined from the shrinkage data presented in Figure 2), and 50°C below and above this temperature, and quenched in air. It was envisaged that quenching of the samples would prevent any second phases present at the temperatures of interest from being reabsorbed into the perovskite. The results were similar to those indicated for calcined powders in Figure 3. Co, Cu and Ni doped materials showed trace amounts (~1 wt%) of SrCrO$_4$ and the V-doped samples revealed the presence of ~4 wt% Sr$_3$(VO$_4$)$_2$. Without evidence for the existence of non-perovskite phases other than SrCrO$_4$ (in LSCCo-1505, LSCCu-1505 and LSCNi-1510) and Sr$_3$(VO$_4$)$_2$ (in LSCV-1505), two hypotheses for the observed sintering behavior might be considered.
The B-site dopants may react with one or more of the other constituent elements (La, Sr and Cr) to form a small amount of second phase, which is below the detection limit of XRD (typically <5wt% second phase). As little as 1 vol% liquid can give rise to enhanced sintering when the liquid is uniformly distributed throughout the sample and the particle size is around 1 μm (15) for the calcined powders in this study varied from 0.8-2.8 μm). Any liquid produced in the doped chromites will be uniformly distributed because of the atomic homogeneity of the liquid forming elements in the perovskite structure.

Interactions between exsolved SrCrO₄ and the B-site dopants were considered most likely. To investigate this possibility, mixtures of 80 mol% SrCrO₄ to 20 mol% Co, Cu, Ni and V (in the form of their respective oxides) were heated to 1150°C and quenched in air for XRD analysis. NiO and CoO showed no interaction with SrCrO₄. CuO transformed into Cu₂O (m.p. 1235°C) but did not react with SrCrO₄. The SrCrO₄ + V₂O₅ mixture formed Sr₃(VO₄)₂, the principle second phase observed in LSCV-1505. Based on this XRD data, reaction of SrCrO₄ with the B-site dopants to form lower melting temperature liquids appears improbable. It may, however, be possible that the B-site elements react with one or both of La and Cr. Hayashi et al. (10) demonstrated that LaCr₀.₉₅Cu₀.₀₅O₃ (without Sr acceptor dopant) exhibited enhanced densification possibly suggesting that an La-Cu-O compound is responsible for the rapid densification phenomenon. An La₂O₃-CuO eutectic occurs at 1025°C (16).

An alternative theory might be that the B-site dopants exhibit a degree of solid solubility in SrCrO₄ making it a more effective liquid sintering aid. Solubility of small amounts of Cu, Co, Ni or V may alter both the viscosity and the wettability of SrCrO₄, and also decrease its melting temperature due to increased system entropy. DTA was conducted on 80-20 mol% ratios of SrCrO₄ to B-site oxides (Figure 4) to determine the effect on the SrCrO₄ melting temperature. The melting points of the individual components are SrCrO₄ (1253°C), CoO (1935°C), CuO (1326°C), NiO (1984°C) and V₂O₅ (690°C). NiO caused no change in the melting point of SrCrO₄, CoO and V₂O₅ additions resulted in a decrease around 20°C, and the trace for SrCrO₄ + CuO indicates a decrease in the SrCrO₄ melting temperature by approximately 45°C. While the B-site dopants do appear to decrease the melting temperature of SrCrO₄, the observed reductions do not correspond to the sintering onset temperatures of the B-site doped LSC-15 samples (Figure 2).

Analysis carried out to date shows no clear indication of the sintering phenomena in B-site doped LSC-15 materials, and it is apparent that significantly more detailed phase analysis, including TEM, is required to establish these densification mechanisms.

Effects of Non-Stoichiometry

Work on LSC-15 (5) without B-site dopants has indicated that non-stoichiometric samples where the A/B site ratio x>1.00 (A-site enriched) exhibit enhanced sintering characteristics compared to A-site depleted (x<1.00) compositions. The mechanisms behind this phenomenon are yet to be fully understood but similar effects were anticipated in the B-site doped LSC-15 compositions. Figure 5 shows density-temperature data for non-stoichiometric B-site doped compositions (La₀.₈₅Sr₀.₁₅)ₓCr₁₋ₓM₉O₃ (0.95≤x≤1.05 and 0.02≤y≤0.10) sintered at 1500°C for 2 hours. The figure also
shows density values for non-stoichiometric LSC-15 without B-site additions sintered at 1600°C for 2 hours to indicate the dramatic effect of A-site enrichment. Unlike LSC-15 without B-site dopant, the compositions investigated in this study show A-site enrichment to have either little positive effect on density or to be particularly detrimental to the sintering behavior, especially for Ni doped compositions. A-site depletion shows reduced densities as observed for non-B-site doped LSC materials. Non-stoichiometric samples were not subjected to further investigation since they indicated no improvement in density compared to the stoichiometric compositions.

**Electrical Conductivity**

Electrical conductivities at 1000°C in air are shown in Table II. It should be noted that the LSC-15 sample was ~75-80% dense and exhibits a lower conductivity value than would be expected for a fully dense sample. The value for LSC-15 in brackets in Table II corresponds to an adjusted value of conductivity assuming zero porosity (6). Co-, Cu- and Ni-doped compositions indicate enhanced electrical conductivity compared to the base material LSC-15. The most stable valencies for copper and nickel are Cu\(^{2+}\) and Ni\(^{2+}\), respectively. Hence, increased electronic conductivity in Cu- and Ni-doped LSC-15 can be simply explained by the charge compensating transition (Cr\(^{3+}\) to Cr\(^{4+}\)) that occurs by doping lower valency cations for Cr\(^{3+}\). Cobalt appears to be the most effective dopant for improving electronic conductivity. However, extended x-ray absorption fine structure (EXAFS) analysis previously conducted on La\(_{0.7}\)Ca\(_{0.3}\)Cr\(_{0.9}\)Co\(_{0.1}\)O\(_3\) (2) indicates that the Co incorporated into the chromite structure is all trivalent (Co\(^{3+}\)). As such it does not act as an acceptor dopant and should not give the conductivity enhancing Cr\(^{3+}\) to Cr\(^{4+}\) transformation. Morelli et al. (17) observed marked increases (greater than one order of magnitude) in electrical conductivity by substituting 15 and 30 mol% Co- for Cr- in Ca-doped LaCrO\(_3\). The enhanced conductivity observed in this present study with only 5 mol% Co-doping is not readily understood, though may not be surprising considering the high electrical conductivity of the perovskite lanthanum cobaltite (LaCoO\(_3\)) (18).

LSCV-1505 shows a decrease in conductivity for two possible reasons. Firstly, V\(^{5+}\) has a higher valency than the Cr\(^{3+}\) that it is replacing. Hence, by placing a 5+ ion into the lattice, existing Cr\(^{4+}\) ions resulting from acceptor doping of Sr\(^{2+}\) for La\(^{3+}\) will transform to their original 3+ valency, thereby reducing electrical conductivity. Secondly, XRD of samples sintered at 1500°C for 2 hours show that Co, Cu and Ni doped LSC materials appear to be (within the detection limits of XRD) phase pure perovskites after sintering, whereas LSCV-1505 indicates the presence of ~3.5 wt% Sr\(_3\)(VO\(_4\))\(_2\), which is not reintroduced into the perovskite at higher temperatures. This implies less than 15 mol% Sr acceptor dopant, a lower proportion of Cr\(^{3+}\) transforming to Cr\(^{4+}\) and subsequently lower conductivity. Mass balance calculations for sintered LSCV-1505 suggest that its actual composition is closer to LSCV-1102 (11 mol% Sr on the A-site and 2 mol% V on the B site) with a slight A-site deficiency (x=0.98) and 3.5 wt% of the second phase, Sr\(_3\)(VO\(_4\))\(_2\).

**Thermal Expansion Behavior**

TEC values (room temperature to 1000°C) are presented in Table II. The TEC of the base material LSC-15 is ~ 9.99 x 10\(^{-6}\) °C\(^{-1}\). V doping has little influence on TEC, Ni and
Cu move the TEC value closer to the target 10.5 x 10^{-6}°C^{-1}, and Co has a dramatic effect pushing the value towards 11.5 x 10^{-6}°C^{-1}.

Table II. Conductivity (at 1000°C) and TEC data (RT-1000°C) in air for L_{0.8}Sr_{0.15}Cr_{1-y}M_{y}O_{3} compositions.

| Composition | Conductivity at 1000°C (S/cm) | TEC (RT-1000°C) (10^{-6}°C^{-1}) |
|-------------|-------------------------------|----------------------------------|
| LSC-15      | 19.9 (21.1)                   | 9.99                             |
| LSCCo-1505  | 39.3                          | 11.44                            |
| LSCCu-1502  | 28.3                          | 10.19                            |
| LSCCu-1505  | 33.4                          | 10.06                            |
| LSCNi-1505  | 32.8                          | 10.12                            |
| LSCNi-1510  | 38.3                          | 10.28                            |
| LSCV-1505   | 20.2                          | 9.93                             |

CONCLUSION

B-site doping of LSC-15 can significantly improve the sinterability of the material. The phenomena responsible for enhanced densification are not yet fully understood, though shrinkage analysis indicates liquid phase sintering processes. Electrical conductivity is increased by doping with Co, Cu and Ni but slightly reduced with V due to the formation of Sr_{3}(VO_{4})_{2}, and lower Sr acceptor doping levels in the chromite. Doping with Cu and Ni provide better TEC matching with the 8-YSZ electrolyte, whereas V has little effect on TEC, and Co doping causes a marked increase in thermal expansion, far exceeding that of the electrolyte.

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Figure 1. Variation of sintered density with temperature for B-site doped La_{0.85}Sr_{0.15}Cr_{1-y}M_yO_3 compositions.
Figure 2. Sintering shrinkage characteristics of La$_{0.85}$Sr$_{0.15}$Cr$_{1-y}$M$_y$O$_3$ compositions.

Figure 3. XRD trace indicating non-perovskite phases present in La$_{0.85}$Sr$_{0.15}$Cr$_{1-y}$M$_y$O$_3$ compositions after calcination at 1000°C for 1 hour.
Figure 4. DTA data for 80-20 mol% mixtures of SrCrO₄ + CoO, CuO, NiO and V₂O₅.

Figure 5. Effects of non-stoichiometry on (La₀.₈₅Sr₀.₁₅)ₓCr₁₋ₓM₂O₃ compositions sintered at 1500°C for 2 hours. La₀.₈₅Sr₀.₁₅CrO₃ (LSC-15) sintered at 1600°C for 2 hours.