

Liquid Phase Sintering of LaCrO_3

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(Received 6 June 1991; revised version received 12 August 1991; accepted 20 August 1991)

Abstract

Solid solutions of $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ were investigated to see if compositions close to LaCrO_3 can be sintered in air at temperatures below 1500°C . The results show that compositions with $0.1 < x < 0.3$ and $0.1 < y < 0.3$ can be sintered to densities above 94% TD in air at 1400°C and below. The improvements in densification result from the formation of a transient liquid phase.

Stability studies were performed by quenching powder samples from 1000°C and an oxygen partial pressure of 10^{-19} atm and subjecting the powders to X-ray diffraction. X-Ray diffraction patterns for $y < 0.30$ showed no second phase, indicating that these compositions are as stable as pure LaCrO_3 towards reduction.

Es wurden feste Lösungen der Zusammensetzung $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ untersucht, um die Frage zu klären, ob Zusammensetzungen in der Nähe von LaCrO_3 bei Temperaturen unterhalb von 1500°C an Luft gesintert werden können. Die Ergebnisse zeigen, daß Zusammensetzungen mit $0.1 < x < 0.3$ und $0.1 < y < 0.3$ bis zu einer Dichte von 94% theoretischer Dichte bei 1400°C und tieferen Temperaturen an Luft gesintert werden können. Die Verbesserung der Verdichtung ergibt sich aus der Bildung einer transienten flüssigen Phase.

Es wurden Stabilitätsuntersuchungen durchgeführt, indem Pulverproben von 1000°C bei einem Sauerstoffpartialdruck von 10^{-19} atm abgeschreckt wurden, wobei die Pulver mittels Röntgendiffraktometrie untersucht wurden. Die Beugungsdiagramme für $y < 0.3$ weisen keine sekundären Phasen auf, so daß diese

Zusammensetzungen hinsichtlich der Reduktion als so stabil wie reines LaCrO_3 angesehen werden können.

Des solutions solides de composition $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ sont étudiées, afin de déterminer s'il est possible de fritter sous air, à des températures inférieures à 1500°C , des compositions proches de LaCrO_3 . Les résultats montrent que les poudres de composition $0.1 < x < 0.3$ et $0.1 < y < 0.3$ peuvent être frittées sous air à des densités supérieures à 94% d_{th} à 1400°C et en dessous. Les progrès en densification résultent de la formation d'une phase liquid transitoire.

On a réalisé des études de stabilité par trempe d'échantillons portés à 1000°C sous une pression partielle d'oxygène de 10^{-19} atm, puis diffraction RX des poudres. Les clichés RX, pour $y < 0.3$, n'indiquent la formation d'aucune phase secondaire, démontrant que ces compositions ont une stabilité comparable à celle de LaCrO_3 face à une réduction.

1 Introduction

In recent years there has been an increasing demand for materials with high electrical conductivity at elevated temperatures. The materials that best meet the requirements are known as perovskites or pseudoperovskites. Such materials have applications in solid oxide fuel cells and thermoelectric devices. The basic perovskite structure is represented by the formula ABO_3 in which A, the large cation site, may be an alkaline-earth or rare-earth ion, and B represents a transition-metal cation. While the ideal perovskite structure is cubic, the majority of the ABO_3 -based compounds deviate slightly from

the cubic structure and form orthorhombic, rhombohedral and tetragonal 'pseudoperovskite' structures. The search for materials that possess the structural stability in a wide range of oxygen activity and high electrical conductivity required in solid oxide fuel cells applications has led to the investigation of a number of solid solutions of candidate perovskites LaBO_3 ($B = \text{Cr, Mn, Fe, Co}$).¹ LaCrO_3 , the most stable of this series, has been the most studied. In the past it has been shown that LaCrO_3 , even with dopants, is difficult to sinter, due to vapor-phase transport of higher-valent oxides of Cr. Typically, the sintering of LaCrO_3 involves temperatures as high as 1775°C and oxygen activities in the 10^{-12} – 10^{-9} range.² For practical applications under such extreme conditions a fabrication is both uneconomical and detrimental to other components which may have to be co-sintered with LaCrO_3 . Thus it would be desirable to process LaCrO_3 at lower temperature in an air atmosphere.

The present authors' recent results on $(\text{La,Sr})(\text{Cr,Mn})\text{O}_3$ have shown that a significant improvement in sinterability was achieved with at least 50 mol% Mn substitution for Cr.¹ However, the substitution of such quantities of Mn on the Cr site has shown two negative effects:

- (1) the electrical conductivity decreased and
- (2) the stability against reduction was diminished.

The present work attempts to improve further the sinterability of LaCrO_3 without adversely affecting its electrical conductivity and stability against reduction.

2 Experimental Procedure

Specimens in the $(\text{La, Ca})(\text{Cr,Co})\text{O}_3$ system were prepared by a polymer precursor method similar to that first described by Pechini.³ The starting chemicals were La and Ca carbonates, and Cr and Co nitrates. All of the chemicals were reagent-grade materials and were standardized by thermogravimetric methods to determine the actual cation contents. The desired compositions were prepared by dissolving measured amounts of selected carbonates and nitrates in solutions of citric acid, ethylene glycol and water. The mixtures were heated on a hot plate at about 95°C until polymerization had occurred. Subsequent heating at higher temperatures resulted in the decomposition of the polymer resin and allowed conversion into the desired oxide. Final calcination was done at 850°C for 8 h. The

resulting powders were milled and subjected to X-ray diffraction to ensure that they were single phase. Powders were pressed into bars with the aid of PVA and water binder. A compaction pressure of 150–250 MPa yielded $0.6 \times 0.4 \times 3.0$ cm bars with density of about 45–52% of theoretical. Densification was conducted over the temperature range 1100 to 1500°C for 2 to 10 h in a SiC heated furnace. Bulk densities of compositions were measured by the liquid (Freon) displacement technique. Scanning electron micrographs of the polished and thermally etched surfaces of sintered specimens were taken in a model JEOLCO JSM-35 scanning electron microscope.

3 Results and Discussion

The primary difficulty of sintering LaCrO_3 -based perovskites in air arises from the volatilization of Cr from the solid at temperatures in excess of 1400°C , causing porosity to develop. This is inhibited by using reducing atmosphere during sintering with oxygen activities of 10^{-10} – 10^{-12} at 1775°C .² Meadowcroft⁴ showed that the sintered density of $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$ increased when excess Sr was added in the form of SrCO_3 before sintering. The maximum beneficial effect was observed when 4–6 mol% SrCO_3 was added. This was probably due to the formation of SrCrO_4 at intermediate temperatures followed by melting and liquid-phase sintering. Flandermeyer *et al.*⁵ used low-melting oxide eutectics as well as La, Y and Mg fluorides at up to 8–10 wt% to increase the sintered density of compacts. In this study the present authors have incorporated various dopants, on both La and Cr sites of the LaCrO_3 , to enhance the sinterability in air. The dopants Ca and Co formed a transient liquid phase which enabled LaCrO_3 to sinter in air at temperatures below 1400°C .

The effect of Co substitution for Cr in LaCrO_3 on densification was studied as a function of Co content and temperature in air. The results are listed in Table 1 and illustrated in Fig. 1. As can be seen for all temperatures, the substitution of Co for Cr improved the sinterability. The sintered density increased sharply when the Co content reached 20 mol%. This may be due to the formation of a liquid phase, since melting was observed at 1500°C for the compositions containing more than 70 mol% Co. This is not surprising, since the reported melting temperature of LaCoO_3 is 1470°C .⁶ These results indicate that the densification was dependent on the amount of Co which was related to liquid-phase

Table 1. Sintered and relative densities as a function of Co content and temperature

Value of y in the composition $\text{LaCr}_{1-y}\text{Co}_y\text{O}_3$	Temperature ($^{\circ}\text{C}$) (sintered for 2 h)									
	1100		1200		1300		1400		1500	
	Density		Density		Density		Density		Density	
	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD
0.0	4.06	60	4.08	61	4.09	61	4.10	61	4.11	61
0.1	4.32	64	4.33	64	4.35	64	4.41	65	4.62	68
0.2	4.80	70	4.93	73	5.23	77	5.50	81	5.73	85
0.5	5.05	72	5.22	75	5.73	82	6.08	87	6.63	95
0.7	5.15	73	5.42	77	5.95	84	6.21	88		Melted
1.0	5.88	82	6.06	84	6.27	94	6.42	95		Melted

content. Therefore the composition with 10 mol% Co showed hardly any densification during sintering. When the Co content was increased to 20 mol% the liquid-phase content at sintering temperatures (above 1200°C) became sufficient, therefore densification took place. An increase in the sintering temperature for compositions with Co content greater than 10 mol% significantly increased the sintered density. For example, the relative density of $\text{LaCr}_{0.8}\text{Co}_{0.2}\text{O}_3$ increased sharply from 70% TD to 85% TD when sintering temperature increased from 1100 to 1500°C . These results indicate that at least 20 mol% Co must be substituted for Cr in LaCrO_3 in order to sinter it in air at temperatures below 1500°C .

The densification of LaCrO_3 and LaCoO_3 was also studied as a function of Ca substitution for La. The substitution of Ca for La in LaCoO_3 significantly increased the sintered density and lowered the melting temperature (see Table 2). Density of 90%

TD was obtained at 1100°C for $\text{La}_{0.70}\text{Ca}_{0.30}\text{CoO}_3$. The substitution of 30 mol% Ca for La in LaCoO_3 lowered the melting temperature from 1470°C to below 1300°C . However, the substitution of Ca for La in LaCrO_3 did not enhance the sinterability at all (see Table 2).

The effect of Ca substitution for La in $\text{LaCr}_{1-y}\text{Co}_y\text{O}_3$ on densification was investigated as a function of Ca content and temperature in air. Tables 2 and 3 and Figs 2 and 3 show the densification behavior of $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ with $x = 0.1, 0.2, 0.3$ and $y = 0.1, 0.2$ as a function of temperature. The additional substitution of Ca for La in $\text{LaCr}_{1-y}\text{Co}_y\text{O}_3$ further enhanced the sintered density. This was probably due to the further decrease in the formation temperature of liquid phase. When the sintering temperature increased from 1200 to 1400°C for $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ with $y = 0.1, 0.2$, a sharp increase in the curves in Figs 2 and 3 was observed. The sharp increase in the

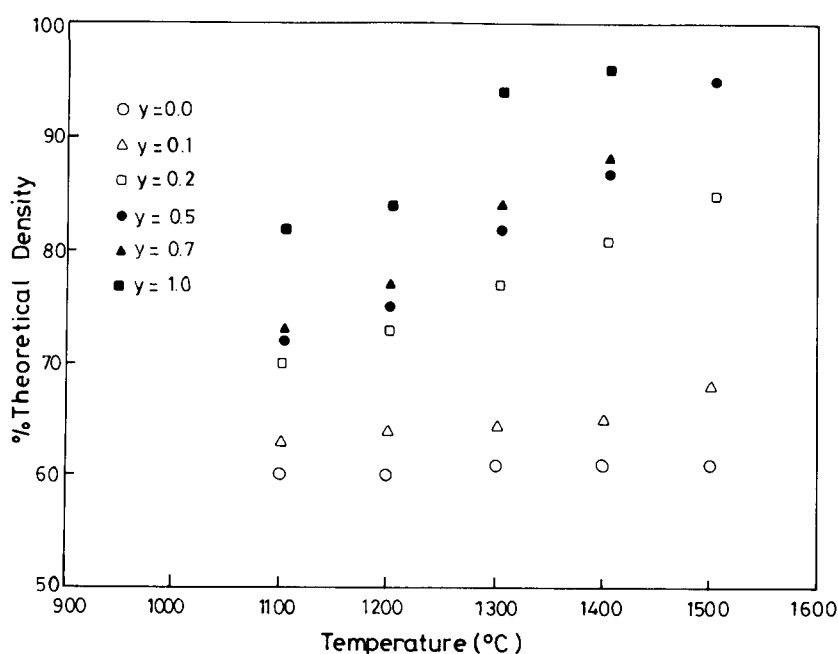
**Fig. 1.** Density of $\text{LaCr}_{1-y}\text{Co}_y\text{O}_3$ as a function of Co content and temperature (sintering time = 2 h).

Table 2. Sintered and relative densities as a function of Ca content and temperature ($y=0.1$)

Value of x in the composition $La_{1-x}Ca_xCr_{0.9}Co_{0.1}O_3$	Temperature ($^{\circ}C$) (sintered for 2 h)									
	1100		1200		1300		1400		1500	
	Density		Density		Density		Density		Density	
	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD
0.0	4.32	64	4.33	64	4.35	64	4.41	65	4.62	68
0.1	4.52	68	4.60	70	5.37	81	5.92	90	6.34	96
0.2	4.82	74	5.13	79	5.87	90	6.11	94	6.22	96
0.3	5.34	83	5.74	89	5.96	93	6.09	95	6.10	95
$La_{0.7}Ca_{0.3}CrO_3$	3.80	62	3.87	62	3.90	63	3.92	63	4.16	68
$La_{0.7}Ca_{0.3}CoO_3$	5.66	89	6.09	95	Melted					

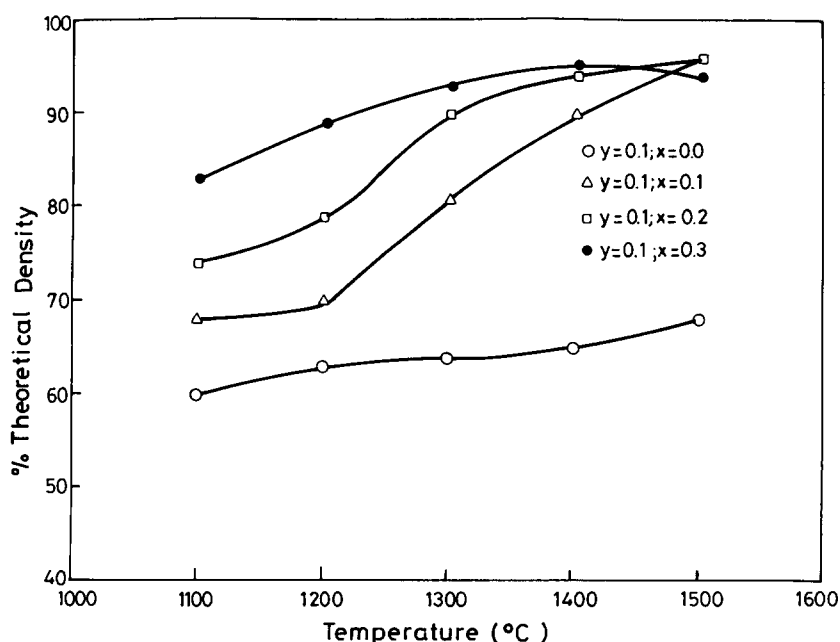
Table 3. Sintered and relative densities as a function of Ca content and temperature ($y=0.2$)

Value of x in the composition $La_{1-x}Ca_xCr_{0.8}Co_{0.2}O_3$	Temperature ($^{\circ}C$) (sintered for 2 h)									
	1100		1200		1300		1400		1500	
	Density		Density		Density		Density		Density	
	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD	g/cm^3	%TD
0.0	4.80	70	4.93	73	5.23	77	5.50	81	5.73	85
0.1	4.75	71	4.80	73	5.69	86	6.03	91	6.11	92
0.2	4.98	76	5.46	83	5.96	91	6.18	94	6.19	94
0.3	5.12	79	5.27	83	5.80	90	6.01	94	6.02	94

sintered density confirmed that the amount of the liquid phase increased as temperature increased. This occurred because the melting temperature of the liquid phase varied as a function of Ca and Co content.

A transient liquid phase is believed to promote sintering due to presence of Ca and Co substitution

on the A and B sites of the perovskite structure, respectively. In the powders prepared for this study X-ray diffraction analysis does not indicate any other phase. This implies that a complete solid solution forms due to similar ionic radii of the substituting ions (Co^{3+} and Cr^{3+}). X-Ray diffraction patterns also revealed the presence of only perov-

**Fig. 2.** Density of $La_{1-x}Ca_xCr_{0.9}Co_{0.1}O_3$ as a function of Ca content and temperature (sintering time = 2 h).

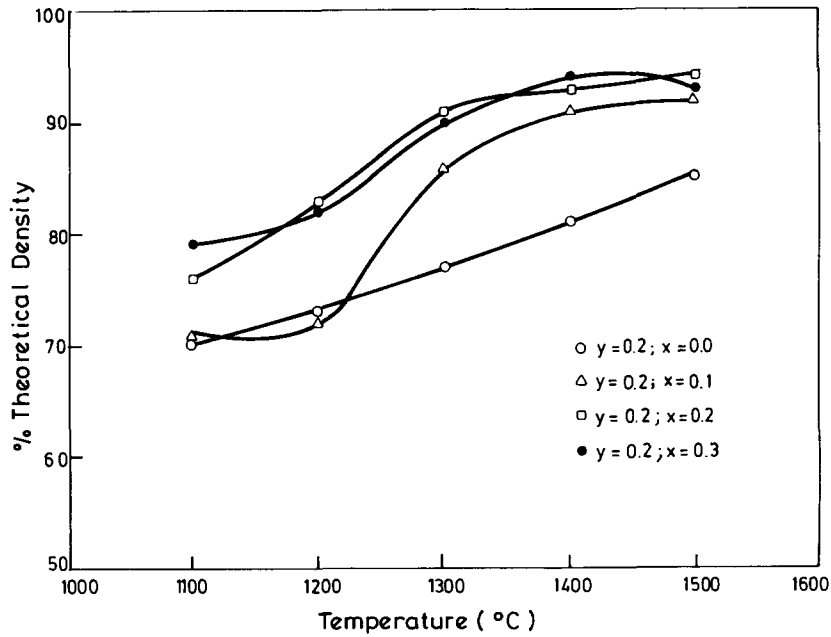
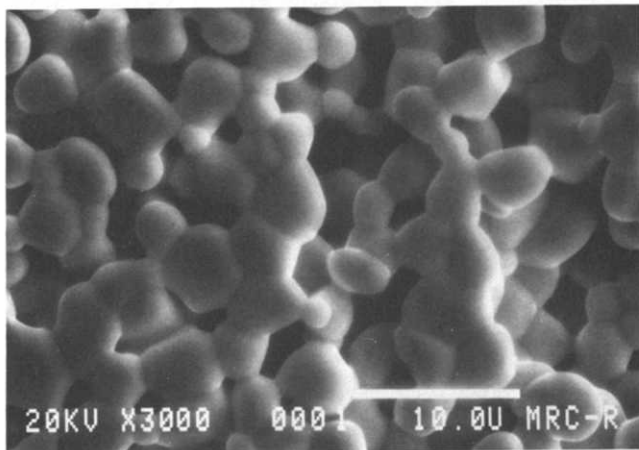
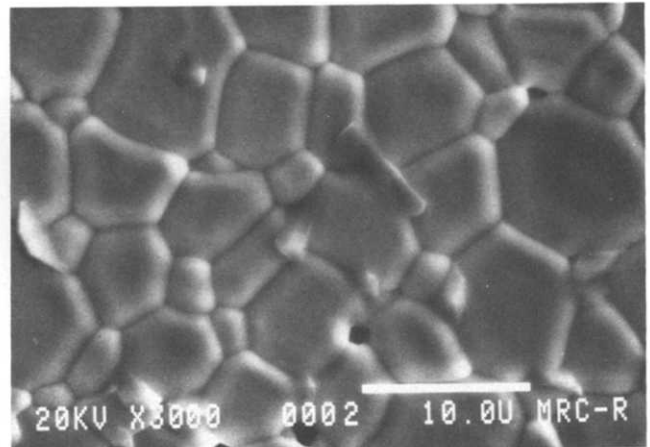


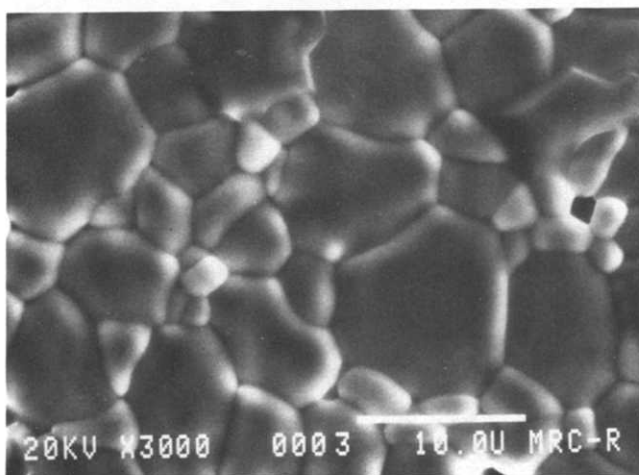
Fig. 3. Density of $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_3$ as a function of Ca content and temperature (sintering time = 2 h).



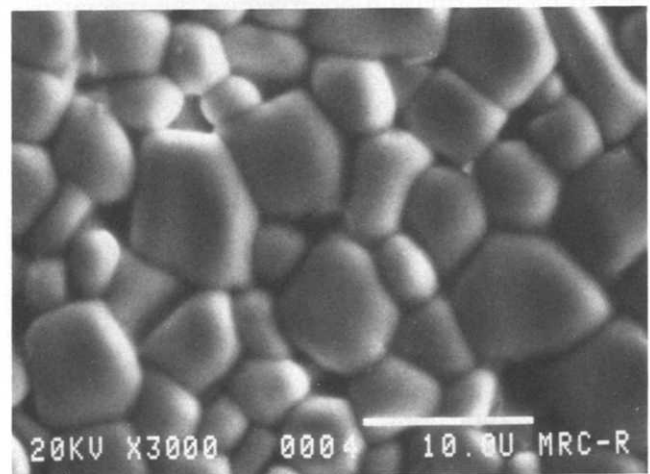
(a)



(b)



(c)



(d)

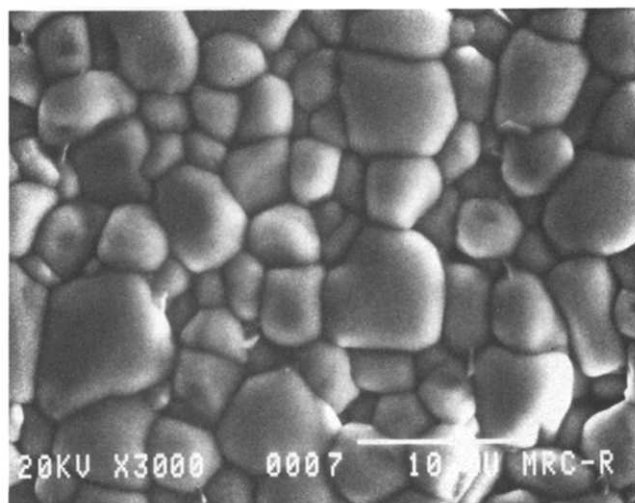
Fig. 4. SEM photomicrographs of the polished and thermally etched surfaces of $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ sintered at 1400°C for 10 h: (a) $x=0.0$; (b) $x=0.1$; (c) $x=0.2$; (d) $x=0.3$.

skite-type structure for all compositions. However, the particles, all of submicron size, were prepared using the Pechini process, and would not be uniform in composition, due to the distribution of Co and Ca ions. Therefore Co- and Ca-rich particles are expected to have melting temperature close to that of Ca-doped LaCoO_3 . Although the X-ray diffraction patterns of Co- and Ca-rich particles and the sample are identical, significant differences were observed in their sintering behavior. The Co- and Ca-rich particles result in the formation of the liquid phase during sintering. The liquid phase also had a high solid solubility in the solid, which meant that the liquid phase was transient and dissipated by forming a solid solution with the major phase. To substantiate that the liquid phase was transient powders with $x=0.2$ and $y=0.2$ were reheated to 1400°C for 10 h and subjected to sintering studies. Sintering studies showed that the powders did not indicate any densification. This occurred because there was no liquid-phase formation during sintering. This must be due to the incorporation of Co- and Ca-rich particles into the major phase and coarsening of the particles during high-temperature reheating. Both processes result in an increase in Cr content in the composition of Co- and Ca-rich particles, explaining the absence of liquid-phase formation during sintering.

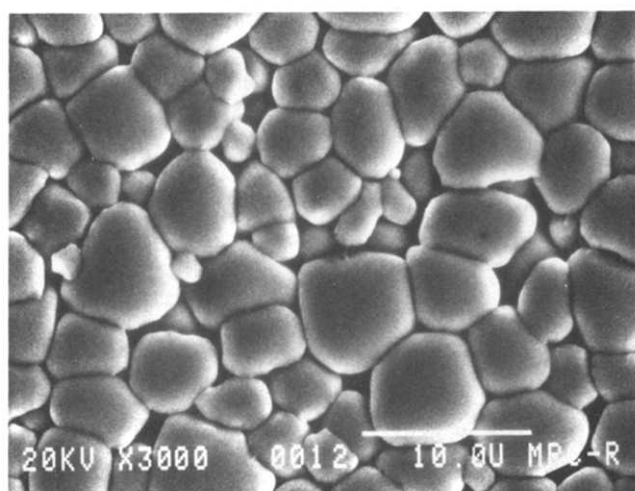
In order to determine the formation temperature of the transient liquid phase, dilatometric studies were made on $\text{La}_{0.80}\text{Ca}_{0.20}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ and $\text{La}_{0.80}\text{Ca}_{0.20}\text{Cr}_{0.80}\text{Co}_{0.20}\text{O}_3$. The shrinkage curves showed that the shrinkage on the specimens started at temperatures above 900°C , but they did not indicate the formation temperature of the liquid phase. However, the presence of the liquid phase was confirmed during the sintering of compositions by the strong deformation observed on the specimens.

In order to explain the effect of the liquid phase, the microstructure of compositions with $x=0.0-0.3$ and $y=0.1-0.3$ was investigated by SEM. SEM photomicrographs of the polished and thermally etched surfaces of specimens sintered at 1400°C for 10 h are given in Figs 4 and 5. Microstructure development with both Ca and Co substitution in LaCrO_3 can be observed from these photomicrographs. As can be seen there are distinct differences in the shape and distribution of grains as a function of Co and Ca content which are related to the fraction of liquid content. If a large liquid content is present, which is the case for compositions with $x>0.1$ and $y>0.2$, complete densification can be achieved by the rearrangement process and no need arises for the solution-precipitation process which

would be expected to change grain shapes.⁷ Consequently the greatest uniformity in grain shape would be expected at high liquid content. Experimentally, microstructures of specimens with high Co and Ca content showed that the grains were rounded, approaching a uniform spherical shape, as seen in Fig. 5. The liquid phase was not continuous at low Co and Ca content, since sharp grain corners and less uniformity in grain shape were observed, due to high volume fractions of solid (see Fig. 4). There is also no indication of a second phase in the microstructures. However, it was obvious that the increasing amount of Co and Ca substitution significantly increased the amount of liquid phase. In order to describe the amount of liquid phase and its distribution, the specimens ($\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_3$) were quenched in air during sintering at 970 , 1080 , 1245 and 1310°C and subjected to microstructural studies. Figure 6 shows microstructures of fractured surfaces of the quenched



(a)



(b)

Fig. 5. SEM photomicrographs of the polished and thermally etched surfaces of $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ sintered at 1400°C for 10 h: (a) $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_3$; (b) $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.7}\text{Co}_{0.3}\text{O}_3$.

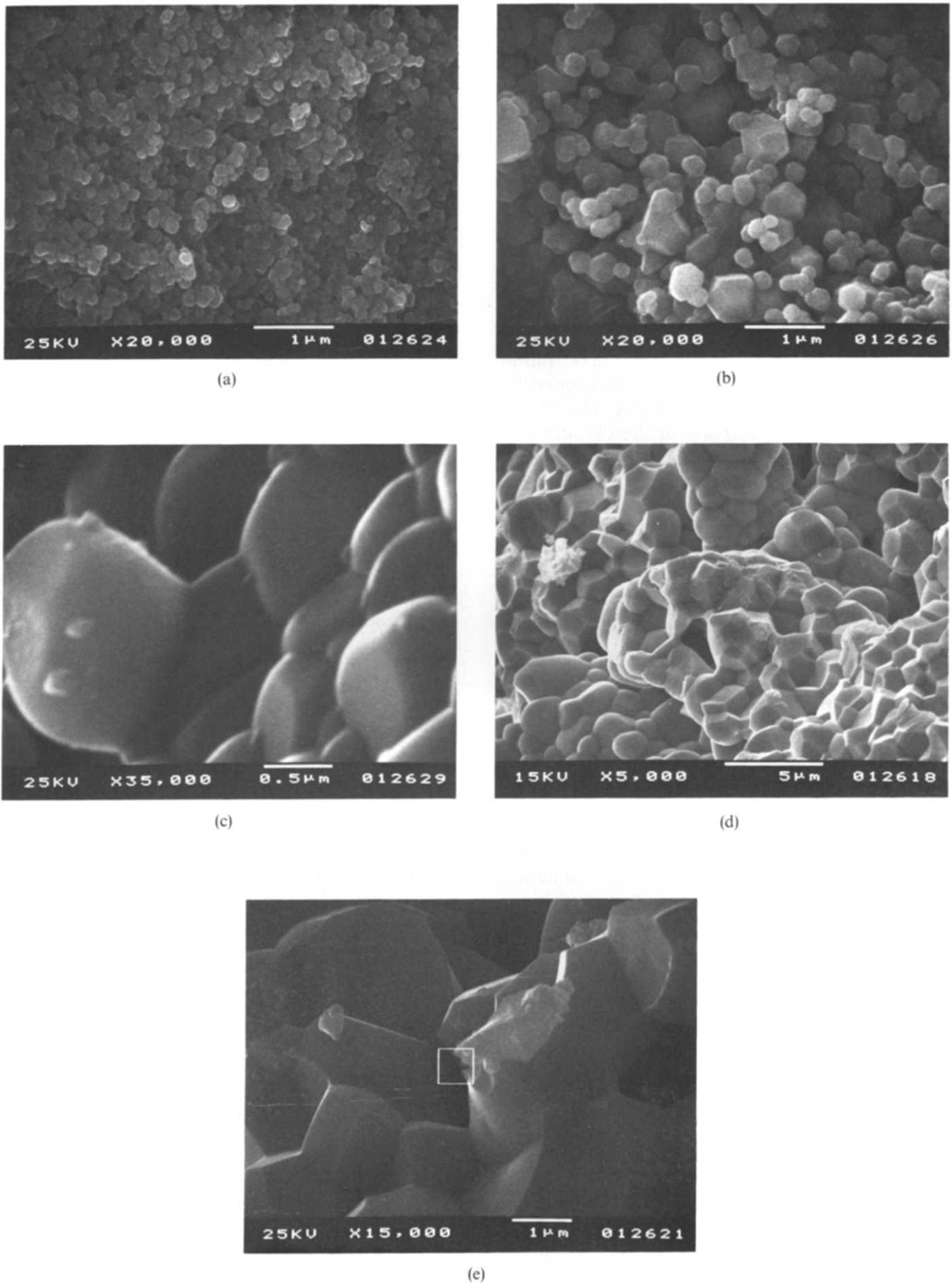


Fig. 6. SEM photomicrographs of fractured surfaces of specimens ($\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_3$) quenched in air from sintering temperatures of (a) 970°C, (b) 1080°C, (c) 1245°C, (d) 1310°C (magnification = $\times 5000$) and (e) 1310°C (magnification = $\times 15\ 000$).

specimens in which the presence of liquid phase is easily observed. The formation of a transient liquid phase during the sintering is evident from microstructural observations.

The results suggest that liquid phase sintering is dominant in the sintering process. The initial stage of liquid-phase sintering typically occurs during the first 10 min after liquid formation.⁸ Both the rate and the degree of densification increase with solid solubility in the liquid. Thus a small amount of liquid phase might be insufficient for densification. To promote sintering in air at temperatures below 1400°C, therefore, at least 10 mol% Co for Cr and 20 mol% Ca for La must be substituted in LaCrO₃. During liquid formation there is rapid initial densification, due to the capillary force exerted by the liquid wetting the solid particles. The results showed that a sharp increase in the densification when the sintering temperature was increased above 1100°C for the compositions. Such a sharp increase in densification can be explained by the starting of a liquid-phase formation just above 1100°C. After liquid forms the solid particles repack under capillary forces because of the wetting liquid. A high sintering temperature is generally useful for the initial stage process, since it increases the solid solubility in the liquid and decreases the viscosity of the liquid.⁸ That explains the further increase in sintered densities with further increase in sintering temperature between 1100 and 1400°C. The processes dominant in the final stage are active throughout the entire liquid-phase sintering cycle; however, because of its slow nature, solid-state sintering is not significant until the final stage of sintering. This manifests itself as a decrease in the densification rate with further increase in sintering temperature, as seen in Figs 2 and 3.

The stability of this system, La_{1-x}Ca_xCr_{1-y}Co_yO₃, towards reduction was investigated by annealing the various compositions at 1000°C in forming gas (90% N₂, 10% H₂, P_{O₂} = 10⁻¹⁹ atm O₂). After annealing for 10–15 h the specimens were quenched in the reducing atmosphere. X-Ray diffraction analysis of quenched specimens showed them to be single phase for all compositions containing y < 30 mol% Co.

4 Conclusions

Powder from the La_{1-x}Ca_xCr_{1-y}Co_yO₃ system with x > 0.1 and y > 0.1 can be densified in air at

temperatures below 1400°C by the formation of a transient liquid phase. The substitution of Co for Cr in LaCrO₃ apparently forms a transient liquid at temperatures below 1500°C, thereby improving sinterability. The additional Ca substitution for La in LaCr_{1-y}Co_yO₃ probably decreases the formation temperature of the liquid, further enhancing sinterability. The composition of the liquid phase is dependent upon the amount of Co and Ca substitution. The liquid phase disperses along the grain boundaries and forms the solid solution with the parent structure. Therefore it does not alter the electrical conductivity and stability of the materials if the Co substitution for Cr is kept lower than 30 mol%, otherwise the stability against reduction at high temperature is diminished. The details of the electrical properties for these materials will be reported in a separate article.

Acknowledgements

This research was sponsored by the US Department of Energy, Basic Science Division. Rasit Koc also received partial support from the Turkish Ministry of Education.

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