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ON THE SYNTHESIS, CHARACTERIZATION, FABRICATION OF COMPONENTS AND PROPERTIES OPTIMIZATION OF PARTIALLY SUBSTITUTED LANTHANUM CHROMITES

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Eight different batches of partially Ba substituted lanthanum chromites were synthesized by a modified liquid route followed by calcination and subjected to systematic characterization. Thin sections of components were made from these chromites by tape casting technique. Optimization of the compositions of the several ingredients to be employed in this fabrication procedure was attempted. The densification data of these powder were also obtained. A brief discussion on the relationship between the chromite processing techniques, their physical properties and component characteristics was attempted from the point of view of their application as bipolar intercell connectors for Solid Oxide Fuel Cells (SOFC).

Keywords: Lanthanum chromites, tape casting and bipolar intercell connectors.

INTRODUCTION

Planar SOFC design offers an attractive choice for realizing higher power densities when compared with the competing designs [1-2]. However, their high operating temperature 1373 K, imposes difficulties to develope suitable components. The bipolar separator material which connects the adjascent single cells should fulfill several requirements: chemical stability, gas tightness, high electrical conductivity and thermal expansion coefficient close to that of the ceramics composing the unit cells. The materials commonly employed as interconnect [3-5] in SOFCs are acceptor doped $LaCrO_2$ and chromium based alloys. MgO is used as dopant in the Westinghouse tubular design [6]. CaO is used as an aid to promote liquid phase sintering [7] and SrO doping was considered by Dornier [8]. The oxide dispersion strengthened alloy $Cr_5Fe_1Y_2O_3$ is employed as metallic interconnect [9-11]. In tune with these investigations and with a view to develop methods of fabrication of thin sections of planar components from doped lanthanum chromites, eight different batches of partially Ba doped (at "La" site) lanthanum chromites were synthesized by modififed liquid route followed by calcination. The powder was subjected to systematic characterization. Thin sections of components were made from these chromites by tape casting technique. Optimization of the compositions of several ingredients to be employed in this fabrication procedure was attempted. The densification data of these powder were obtained. A brief discussion on the relationship between the chromite processing techniques, their physical properties and component characteristics was examined from the point of view of its application as bipolar intercell connectors for the SOFCs.

EXPERIMENTAL

Synthesis of oxide powder

Aqueous solutions of lanthanum carbonate and chromium oxide were prepared with appropriate molecular weights. Dilute nitric acid was employed to dissolve the chromium oxide. These two solutions were mixed intimately. Then a 1:1 molar weighed quantities of ethylene glycol and citric acid were added to the above solution in steps, alternatively with constant stirring. The whole mass was heated on a steel tray at 363 K until the mass becomes very reactive and turns into black resin like stuff. The resulted mass was made into powder, and sintered in air on alumina boats in a programmable furnace for different durations.

By this technique, $La_{(1-x)}Ba_xCrO_3$, where x = 0.1, 0.2, 0.3, 0.5 and 0 were prepared. Similarly, $La_{(1-x)}Ba_{x+a}CrO_3$, where a = 0.01, 0.02, 0.05 and x as above were also prepared.

Characterization of the oxides

The density values of the Ba doped lanthanum chromite powder as a function of Ba content in the chromite and as

TABLE I: The density values of "Ba" doped lanthanum chromites

Sample	Density (g/cc)			
	As prepared	Sintered 925/24 h	Sintered 1400/5 h	Sintered 925/24 h & 1400/5 h
$LaCrO_3$	3.4306	6.7094	6.6531	6.6456
$La_{0.9}Ba_{0.1}CrO_3$	3.3907	6.4974	6.5623	6.5542
$La_{0.8}Ba_{0.2}CrO_3$	3.3591	6.4557	6.4201	6.4164
$La_{0.7}Ba_{0.3}CrO_3$	3.3529	5.9594	5.9326	5.9032
$La_{0.5}Ba_{0.5}CrO_3$	3.3462	5.5801	5.5743	5.5405
$La_{0.9}Ba_{0.11}CrO_3$	3.3701	6.4968	6.5607	6.5538
$La_{0.9}Ba_{0.12}CrO_3$	3.3696	6.4943	6.5590	6.5523
$La_{0.9}Ba_{0.15}CrO_3$	3.3675	6.4921	6.5572	6.6504

a function of processing variables were measured and are presented in Table I. The density measurements were carried out in a Micromeritics Accu Pyc 1330 density meter in He atmosphere. The listed values are the mean obtained from three measurements.

TABLE II: The particle size distribution of chromite powder

Sample	Particle size distribution (μm)	
	Diameter at 10%	Diameter at 90%
$LaCrO_3$/925/24 h	1.02	69.31
$LaCrO_3$/1400/5 h	8.01	321.56
$LaCrO_3$/925/24 h; 1400/5 h	8.28	338.13
$La_{0.9}Ba_{0.1}CrO_3$/925/24 h	1.43	69.31
$La_{0.9}Ba_{0.1}CrO_3$/1400/5 h	4.47	398.90
$La_{0.9}Ba_{0.1}CrO_3$/925/24 h; 1400/5 h	4.68	394.74
$La_{0.8}Ba_{0.2}CrO_3$/925/24 h	8.77	274.96
$La_{0.8}Ba_{0.2}CrO_3$/1400/5 h	9.01	321.56
$La_{0.8}Ba_{0.2}CrO_3$/925/24 h; 1400/5 h	9.45	434.73
$La_{0.7}Ba_{0.3}CrO_3$/925/24 h	0.49	56.69
$La_{0.7}Ba_{0.3}CrO_3$/1400/5 h	2.00	452.03
$La_{0.7}Ba_{0.3}CrO_3$/925/24 h; 1400/5 h	2.32	470.86
$La_{0.7}Ba_{0.3}CrO_3$/925/24 h	1.40	104.67
$La_{0.7}Ba_{0.3}CrO_3$/1400/5 h	8.40	304.64
$La_{0.7}Ba_{0.3}CrO_3$/925/24 h; 1400/5 h	8.78	431.78
$La_{0.9}Ba_{0.11}CrO_3$/925/24 h	0.77	63.28
$La_{0.9}Ba_{0.11}CrO_3$/1400/5 h	1.76	369.97
$La_{0.9}Ba_{0.11}CrO_3$/925/24 h; 1400/5 h	4.54	473.43
$La_{0.9}Ba_{0.12}CrO_3$/925/24 h	1.72	93.23
$La_{0.9}Ba_{0.12}CrO_3$/1400/5 h	10.58	387.97
$La_{0.9}Ba_{0.12}CrO_3$/925/24 h; 1400/5 h	10.76	395.20
$La_{0.9}Ba_{0.15}CrO_3$/925/24 h	1.43	79.76
$La_{0.9}Ba_{0.15}CrO_3$/1400/5 h	3.32	385.43
$La_{0.9}Ba_{0.15}CrO_3$/925/24 h; 1400/5 h	5.89	498.76

The particle size distribution of the chromite powder was measured as a function of Ba content in the chromite and as a function of processing variables with the help of a Cilas Granulometer 1064 No.085 in isopropyl alcohol. The data obtained are presented in Table II.

The formation of the desired chromite phase with specific composition was ensured by x-ray powder diffraction data. The unit cell constants were also worked out for the chromites as a function of Ba content. The obtained data are presented in Table III.

The chromite powder was subjected to uniaxial pressing to form discs using isopropyl alcohol as binding agent. Different discs were fabricated as a function of pressing pressure. The presure values employed were 10000 psi, 12000 psi and 15000 psi for one min duration. The discs thus obtained were sintered at in air for 5 hour.

Fabrication of thin sections of tapes was done by dispersing the chromite into solvent/binder/plasticizer. The mixture was mixed throughly in a vibratory mill for 1 h and subjected to deaeration. Then again mixed in a ball mill for 24 h. The resulting slurry was cast into tapes in a tape casting machine. These tapes were dried in air in order to burn out the organic ingredients. Then they were subjected to programmed sintering in a programmable furnace. The ratio of binder to chromite was in the range 0.12 - 0.22. The ratio of plastisizer to binder was 0.2 - 0.35.

The surface microstructural features of the sintered tapes and discs were obtained by SEM and the pictures are shown in Fig. 1. The thermal expansion characteristics of the fabricated chromite tapes were obtained in a Dilatometer [Theta Industries].

RESULTS AND DISCUSSION

Density measurements

The chromite powder prepared by the modified liquid route was very fine. The density values of the chromite powder as prepared, powder sintered at 1198 K for 24 h duration, powder sintered at 1673 K for 5 h duration and powder

TABLE III: XRD unit cell constants for chromite powder

Sample	a(Å)	b(Å)	c(Å)
$LaCrO_3$	5.478	5.454	7.714
$La_{0.9}Ba_{0.1}CrO_3$	5.466	5.448	7.762
$La_{0.8}Ba_{0.2}CrO_3$	5.451	5.436	7.651
$La_{0.7}Ba_{0.3}CrO_3$	5.450	5.431	7.628
$La_{0.5}Ba_{0.5}CrO_3$	5.260	5.252	7.619
$La_{0.9}Ba_{0.11}CrO_3$	5.471	5.448	7.712
$La_{0.9}Ba_{0.12}CrO_3$	5.479	5.442	7.721
$La_{0.9}Ba_{0.15}CrO_3$	5.481	5.450	7.718

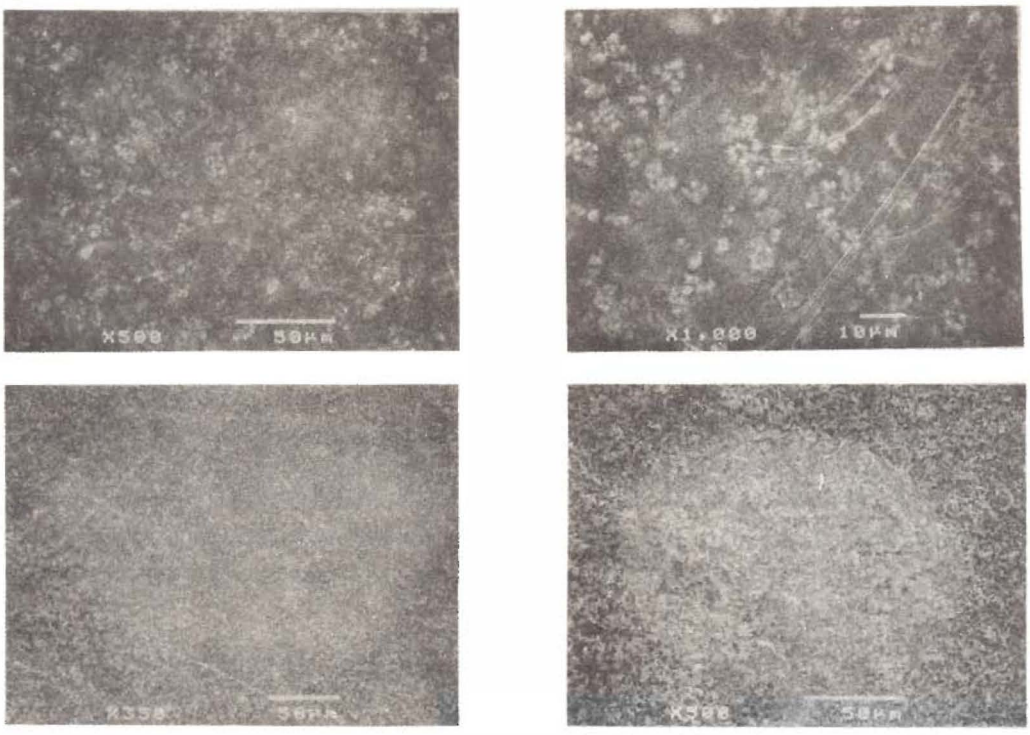

Fig. 1: The microstructural features of the thin sections of $La_{0.9}Ba_{0.1}CrO_3$ tapes (a & b)/sintered discs (c&d)
(a) The top surface - 500 times magnification (b) The top surface - 1000 times magnification
(c) Pressed at 15000 psi for min duration and sintered at 1673 K for 5 h duration - 350 times magnification
(d) Same as in "c" with 500 times magnification

sintered at 1198 K for 24 h followed by 1673 K for 5 h duration revealed that as the Ba content was increased, the density of the chromite powder decreased even prior to and after sintering. The density values showed a further decrease as the sintering temperature and the sintering duration were increased.

Particle size distribution

The particle size distribution analysis data obtained on the chromites indicated that the particle diameter of more than 90% of the bulk powder remained uniform. It was also noticed that the particle diameter values of chromite increased as the sintering temperature was increased.

X-ray diffraction data

The x-ray powder diffraction data obtained on the chromites indicated that the crystal structure of all the Ba partially substituted chromites was orthorhombic with very little difference in their unit cell constants.

Density values of sintered chromite pellets

The densification data obtained on the chromites indicates that the density values of the sintered pellets increased as a function of the pressing pressure values. Further it was observed that the densification of partially Ba substituted lanthanum chromites was more for the pellets which had a little excess of Ba at the La site.

Surface microstructure of the tapes and pellets

The microstructural features of the surface of the thin sectiions of tapes indicated the uniform distribution of the particles such as binder, plasticizer and chromites. The mechanical strength of these sections of tapes was very good although the thickness was about 100 microns. Tapes with thickness less than 100 microns were also fabricated and sintered. Very thin, porous and uniform tapes could be fabricated in these investigations.

The microstructural features of the sintered pellets revealed very uniform distribution of grains. The distribution of fine grains of chromite was very uniform and regular when the pellets were pressed at 15000 psi.

Thermal expansion characteristics

The sintering shrinkage values and the coefficient of thermal expansion values obtained on partially Ba substituted lanthanum chromite tapes as a function of Ba content in the chromite is shown in Fig. 2. The sintering shrinkage values and the coefficient of thermal expansion values obtained on partially Ba substituted lanthanum chromite pellets as a function of Ba content in the chromite is shown in Fig. 3.

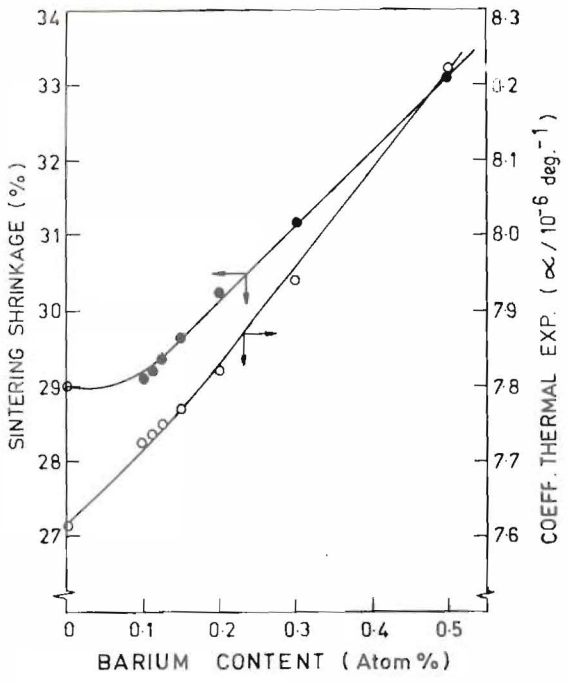

Fig. 2: Sintering shrinkage values and coefficeint of thermal expansion values of chromite tapes Binder/ceramic = 0.21 Plasticizer/binder = 0.2

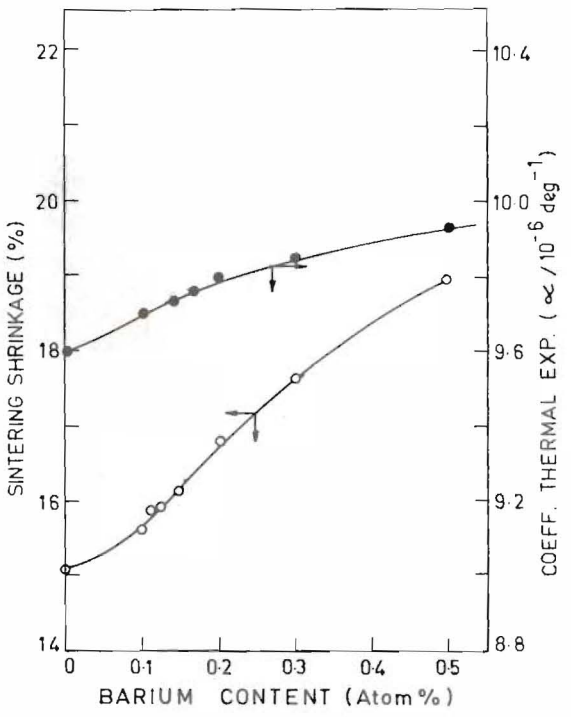

Fig. 3: Sintering shrinkage values and coefficient of thermal expansion values of chromite discs pressed at 15000 psi for 1 min duration

It was observed that as the Ba content in the chromite increased the coefficient of thermal expansion values and the percentage shrinkage values almost attain a limiting value in the case of sintered pellets when the Ba content at the La site of the chromite was 0.5 and above. This was not so in the case of thin sections of tapes. In the case of tapes it was observed that the sintering shrinkage values and the coefficient of thermal expansion values did not attain a limiting value even for chromite compositions containing Ba above 0.5. It also observed that the firing shrinkage values in percentage increased as a function of the increase in the ratio between the weight of binder to the weight of chromite when the ratio between the weight of the plasticiser and the binder was kept at 0.2.

CONCLUSION

It was concluded that thin sections of components and dense pellets with reproducible functional characteristics can be very well fabricated for application in high temperature devices from partially Ba substituted lanthanum chromites.

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