

Sinterability and electrical conductivity of calcium-doped lanthanum chromites

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Calcium-doped lanthanum chromites, $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$, have been synthesized to investigate effects of calcium doping on sinterability and electrical conductivity. X-ray diffractometric results have revealed that in addition to normal perovskites ($\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$), chromium-deficient perovskites can exist as a single phase in the composition region $0.1 < x < 0.3$, although the deficit of chromium is small. These chromium-deficient perovskites show a good sinterability even in air at 1873 K. Electrical conductivity of these perovskites has been measured as functions of temperature and oxygen potential. It has been found that electrical conductivity of the chromium-deficient perovskites increases almost linearly with total calcium content. The magnitudes of electrical conductivity are comparable to those of strontium-doped lanthanum chromites.

1. Introduction

The alkali-earth-doped lanthanum chromite has good electrical conductivity and chemical stability at both reductive and oxidative atmospheres. This material has been applied for use as interconnectors of solid oxide fuel cells (SOFC) [1]. However, lanthanum chromite does not sinter well without doping with other transition metals (Cu, etc.) [2] nor without using a hot-pressing technique [3]. In SOFC, it is necessary to find an appropriate way of fabricating a gas-tight interconnector of lanthanum chromite. Isenberg developed an electrochemical vapour deposition technique (EVD) at a reductive atmosphere to make a tubular cell [4]. Recently, Flandermeyer *et al.* [5] found some sintering aids for lanthanum chromites such as fluorides to co-fire a monolithic cell. We are interested in developing a planar SOFC. To construct such a cell, we feel that these two methods are not appropriate.

During investigations on calcium-doped lanthanum chromite, we found that slightly chromium-poor perovskites give rise to considerable improvement of sinterability without any sintering aids even in air. We succeeded in the fabrication of dense gas-tight plates by sintering lanthanum chromite films by a doctor blade method. This paper reports the composition dependence on the sinterability and the electrical conductivity of these calcium-doped lanthanum chromites.

2. Experimental procedure

2.1. Sample preparation

Nineteen samples, of different compositions as given in Table I, were prepared. To express the composition of the samples, the form $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$ is adopted for convenience, where y is a nominal

chromium deficit. Samples were prepared by the following method; $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ powder was dissolved in an excess amount of ethanol, and La_2O_3 and CaCO_3 powders were added and stirred for about 1 h. After complete gelling, the mixture was dried at 723 K in air, and then ground and calcined in air at 1273 K for 4 h; products were identified by X-ray diffractometry (XRD). When $y = 0$ (samples 1 to 5), a perovskite structure existed as a single phase in samples 1 to 3 ($0 < x < 0.2$), whereas in the region of $x \geq 0.3$ (samples 4 and 5), a small amount of CaCrO_4 phase was detected. In the composition region $y > 0$ (samples 6 to 19), La_2CrO_6 as well as CaCrO_4 was always detected, and in amounts increasing with the chromium deficit (y).

2.2. Sintering process

The calcined powders of $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$ were pressed into pellets (20 mm diameter and 2 mm thick) under 150 MPa. Pellets were finally sintered in air at 1873 K for 5 to 10 h. X-ray diffraction (XRD) results indicated that sintered samples consisted only of a perovskite phase in the region of $y < 0.04$. When the value of the chromium deficit (y) was above 0.05, CaO and/or La_2O_3 phases were detected; some samples were disintegrated because of the hygroscopic nature of La_2O_3 (shown in Table I). Samples 6 and 7 were also disintegrated, although no second phases were detected in the XRD results. The observed phase relations in the $\text{CaO}-\text{Cr}_2\text{O}_3-\text{La}_2\text{O}_3$ system are summarized in Fig. 1.

The relative density (sinterability) was calculated from the experimental lattice parameter, weight, and size of the sample. Lattice parameter decreased with

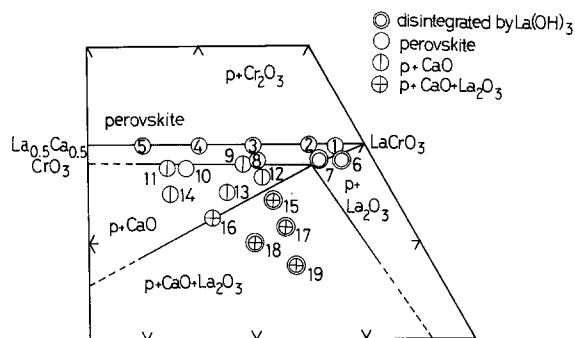


Figure 1 Phase diagram of the CaO-Cr₂O₃-La₂O₃ system at 1873 K: XRD results of prepared samples are shown as symbols.

calcium content (in Fig. 2), and the orthorhombic cell seemed to become cubic for $x = 0.50$: this behaviour is similar to the results which were reported by Berjoan *et al.* [6].

2.3. Electrical conductivity measurement

Samples were cut to the dimensions $\sim 16 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$, and placed in an alumina tube. Electrical conductivity was measured by a four-probe method. The first series measurements was made in air from 770 to 1400 K. Temperature was measured using Pt/Pt-13% Rh thermocouples attached to the sample tube. The second series of measurements were made as a function of oxygen partial pressure, which was regulated by flowing gas mixtures of O₂-Ar (for $P(\text{O}_2) = 10^{-1}$ to 10^{-3} bar), H₂-CO₂ ($P(\text{O}_2) = 10^{-3}$ to 10^{-15} bar), or H₂-H₂O ($P(\text{O}_2) < 10^{-15}$ bar), and monitored by a ZrO₂ sensor.

3. Results

Fig. 3 shows the effect of calcium doping ($x + y$) on sinterability at 1873 K for 5 to 10 h. Non-chromium-deficient samples ($(\text{La}_{1-x}\text{Ca}_x)\text{CrO}_3$, $y = 0$) showed quite low densification, and with increasing calcium content, relative density (d/d_0) increased and finally

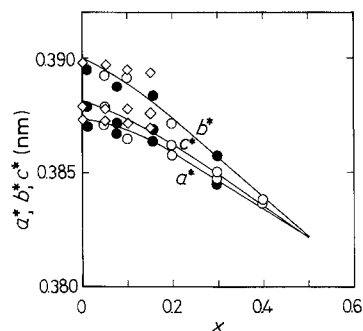


Figure 2 Lattice parameters, a^* , b^* , and c^* of $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$ as a function of calcium content (x): (○) $y = 0$; (●) $y > 0$; (◇) Song *et al.* [3] ($y = 0$); (—) Berjoan *et al.* [6] ($y = 0$). $a^* = a/2^{1/2}$, $b^* = b/2^{1/2}$, $c^* = c/2$; where a , b and c are lattice parameters of the orthorhombic cell.

approached 0.95 at $(x + y) = 0.40$ (sample 5). It should, however, be noted that chromium-deficient samples ($y > 0$) exhibited high densification of $d/d_0 = 0.90$ to 0.94 independently of calcium content: the densities of some samples were measured by Archimedes method, resulting in higher values of $d/d_0 = 0.94$ to 0.97 .

Fig. 4 shows relative density plotted as a function of chromium deficit. A drastic change in the region of $y = 0$ to 0.03 suggests that only a slight deficiency of chromium is enough to improve densification of lanthanum chromite in air. Non-coloration of alumina plates on which these samples had been placed indicated that these chromium-deficient lanthanum chromites had weak volatility of chromium component during sintering.

Fig. 5 shows the temperature dependence of electrical conductivity of $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$ in a plot of $\log(\sigma T)$ against $1/T$. Several authors reported that linear dependence in this plot is characteristic of the small polaron hopping transport mechanism [7, 8], and similar results were obtained in this study. The

TABLE I Nominal compositions of samples investigated and their final phases after sintering at 1873 K

Sample number	Composition				XRD results at 1873 K	Remarks
	La(1 - x)	Ca(x)	Cr(1 - y)	Ca(y)		
1	0.950	0.050	1.000	0	p*	
2	0.900	0.100	1.000	0	p	
3	0.800	0.200	1.000	0	p	
4	0.700	0.300	1.000	0	p	
5	0.600	0.400	1.000	0	p	
6	0.974	0.026	0.974	0.026	p	disintegrated [†]
7	0.923	0.077	0.974	0.026	p	disintegrated [†]
8	0.821	0.179	0.974	0.026	p	
9	0.800	0.200	0.960	0.040	p + CaO	
10	0.700	0.300	0.950	0.050	p	
11	0.667	0.333	0.952	0.048	p + CaO	
12	0.842	0.158	0.947	0.052	p + CaO	
13	0.800	0.200	0.900	0.100	p + CaO	
14	0.700	0.300	0.900	0.100	p + CaO	
15	0.889	0.111	0.889	0.111	p + CaO + La ₂ O ₃	disintegrated
16	0.800	0.200	0.850	0.150	p + CaO + La ₂ O ₃	
17	0.941	0.059	0.823	0.177	p + CaO + La ₂ O ₃	disintegrated
18	0.900	0.100	0.800	0.200	p + CaO + La ₂ O ₃	disintegrated
19	1.000	0	0.750	0.250	p + CaO + La ₂ O ₃	disintegrated

*p: perovskite phase of $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$.

[†]Two pellets were prepared: one was disintegrated, and the other kept its stability in electrical conductivity measurements.

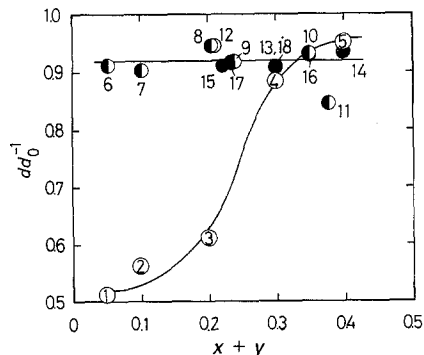


Figure 3 Effect of calcium content on relative density for $(La_{1-x}Ca_x)(Cr_{1-y}Ca_y)O_3$ at 1873 K in air: (○) $y = 0$; (●) $0 < y \leq 0.05$; (●) $y > 0.05$.

slopes of lines are almost the same among the samples investigated.

The electrical conductivity at 1273 K is shown in Fig. 6 plotted as a function of combined calcium content ($x + y$). For the case of $0 < y < 0.05$, electrical conductivity depends almost linearly on calcium content. This linear dependence can be well interpreted in terms of the formation of holes, the concentration of which increases linearly with calcium content. Samples 13, 14 and 16 ($y > 0.05$) showed lower conductivity than this line, probably because of the formation of La_2O_3 or CaO at the grain boundary. Samples 2 and 3 also showed lower conductivity, apparently because of their low relative densities. It is noticed that sample 4 showed significantly higher conductivity than chromium-deficient samples.

Fig. 7 shows the oxygen potential dependence on electrical conductivity of $(La_{1-x}Ca_x)(Cr_{1-y}Ca_y)O_3$ at 1416 and 1273 K. Three samples which had only one perovskite phase were selected. Samples of low calcium content had a flat region of conductivity, and their conductivity decreased at reductive atmospheres. On the other hand, the heavily doped sample did not have a flat region and its conductivity gradually decreased with decreasing oxygen potential. At higher temperatures (1416 K), their conductivities started to decrease at higher oxygen potentials.

4. Discussion

The present investigation has revealed that slightly chromium-deficient perovskites have good sinterability and high electrical conductivity.

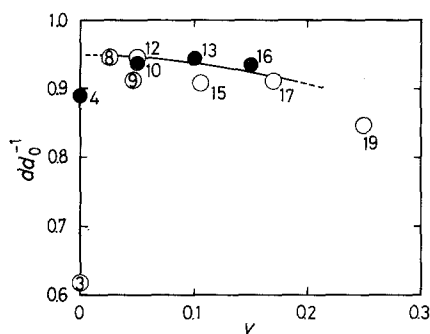


Figure 4 Effect of chromium deficit on relative density for $(La_{1-x}Ca_x)(Cr_{1-y}Ca_y)O_3$ at 1873 K in air: (○) $0.20 \leq (x + y) \leq 0.25$; (●) $0.30 \leq (x + y) \leq 0.35$.

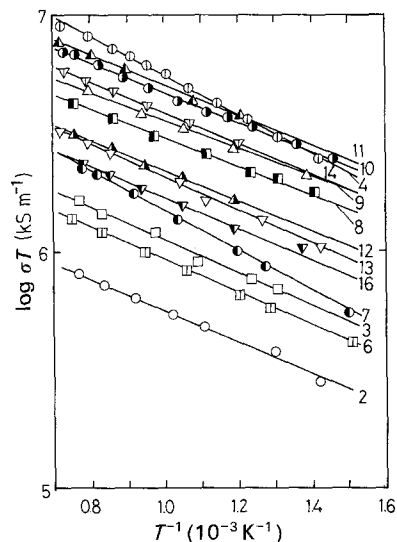


Figure 5 Temperature dependence of electrical conductivity for $(La_{1-x}Ca_x)(Cr_{1-y}Ca_y)O_3$. The number of each line corresponds to the sample number listed in Table I.

In previous investigations, several authors reported that it is difficult to densify lanthanum chromite perovskites in an oxidative atmosphere because of the volatilization of chromium components [9–12]. Matsumoto and Sata [9] reported that calcium doping enhanced volatilization of chromium components; this fact implies that heavy calcium doping causes bad sinterability. However, we found that heavily calcium-doped lanthanum chromites (samples 4 and 5) show high densification in spite of volatilization of chromium components (Fig. 3), which is in conflict with Matsumoto and Sata's interpretations. Meadowcroft [13] also reported that heavy doping of strontium enhanced densification of lanthanum chromite, and Bansal *et al.* [14] found that its relative density increased with sintering time. Here, we would like to emphasize the following points. The heavily doped lanthanum chromites have some possibility of changing their composition to the chromium-poor side during sintering because of the volatilization of CrO_3 , and this chromium deficiency seems to have a good effect on the densification of lanthanum chromite. This consideration is supported by our results that chromium-deficient lanthanum chromites show high densification and low CrO_3 volatility.

Three possible phenomena associated with the

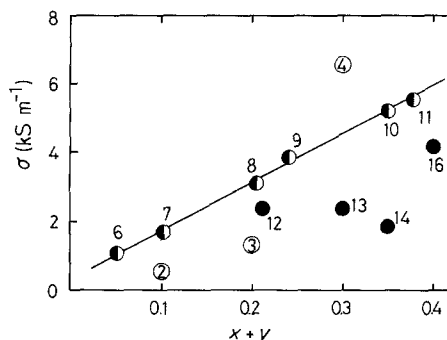


Figure 6 Compositional dependence of electrical conductivity for $(La_{1-x}Ca_x)(Cr_{1-y}Ca_y)O_3$ at 1273 K: (○) $y = 0$; (●) $0 < y \leq 0.05$; (●) $y > 0.05$.

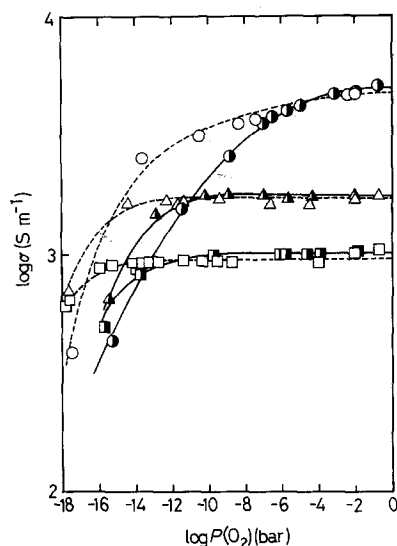


Figure 7 Oxygen partial pressure dependence of electrical conductivity for $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$ at $(\blacksquare, \blacktriangle, \bullet)$ 1416 and $(\square, \triangle, \circ)$ 1273 K: (\bullet, \circ) $(\text{La}_{0.700}\text{Ca}_{0.300})(\text{Cr}_{0.950}\text{Ca}_{0.050})\text{O}_3$ (sample 10); $(\blacktriangle, \triangle)$ $(\text{La}_{0.923}\text{Ca}_{0.077})(\text{Cr}_{0.974}\text{Ca}_{0.026})\text{O}_3$ (sample 7); (\blacksquare, \square) $(\text{La}_{0.974}\text{Ca}_{0.026})(\text{Cr}_{0.974}\text{Ca}_{0.026})\text{O}_3$ (sample 6).

chromium deficiency in the perovskite structure can be considered. (1) The formation of chromium site vacancy; (2) the substitution of calcium for chromium site; (3) the precipitation of CaO or La_2O_3 in a small but undetectable amount. Because chromium has a low coordination number (6), it may be difficult to form a chromite site vacancy in the perovskite structure. On the other hand, the calcium substitution (for the chromium site) or the precipitation of CaO or La_2O_3 appears more probable, although we have not obtained any evidence from the lattice parameter changes among the samples. In any case, the microscopic role of chromium deficiency remains uncertain.

Meadowcroft reported similar phenomena for the strontium-doped samples. He added small amounts of SrCO_3 to the stoichiometric lanthanum chromites (LaCrO_3). These samples showed higher sinterability than normal strontium-doped samples ($\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$). However, all these samples were found to be disintegrated because of the formation of $\text{La}(\text{OH})_3$ [13]. According to the results of Meadowcroft [13], $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ perovskite single-phase region comes into contact with perovskite- La_2O_3 two-phase region for $0 < x < 0.3$ in the $\text{SrO}-\text{Cr}_2\text{O}_3-\text{La}_2\text{O}_3$ system. Therefore, a slight deficiency of chromium brings about precipitation of La_2O_3 . On the other hand, our results reveal that perovskite single-phase region comes into contact with perovskite- La_2O_3 two-phase region for $0 < x < 0.1$ in the $\text{CaO}-\text{Cr}_2\text{O}_3-\text{La}_2\text{O}_3$ system, and for $x > 0.1$, the large deficiency of chromium causes CaO precipitation. This CaO did not exert any bad influence upon the chemical stabilities of the samples at room temperature. These features have been examined by thermodynamical analysis, and detailed results will be published elsewhere [15].

The results of electrical conductivity measurements suggest that the samples of the $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$

series have electrical conductivities that are comparable with that of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ [12] and are higher than that of $\text{LaCr}_{1-y}\text{Mg}_y\text{O}_3$ measured by Flandermeier *et al.* [16]. Furthermore, Fig. 6 shows clearly that the non-chromium-deficient composition sample gave a higher electrical conductivity than chromium poor samples at $x = 0.3$ (sample 4). These results imply that highly densified samples of non-chromium-deficient perovskites ($\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$) may exhibit higher conductivity than strontium-doped perovskites.

5. Conclusion

The slight chromium deficiency in calcium-doped lanthanum chromite showed a possibility of obtaining dense samples which also have sufficient chemical stability in air. These chromium-deficient perovskites also have electrical conductivities high enough for use in SOFC interconnectors. It is necessary to obtain chemically stable and sinterable samples to make use of lanthanum chromite as a component of planar SOFC. The present investigation revealed that chromium-deficient perovskites $(\text{La}_{1-x}\text{Ca}_x)(\text{Cr}_{1-y}\text{Ca}_y)\text{O}_3$ show some feasibility for use in SOFC interconnectors. It is hoped to undertake further investigation into the detailed composition dependence of sinterability and effects of chromium-deficiency on electrical conductivity. Thermal properties such as thermal expansion coefficient are now being investigated.

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