Self-propagating high-temperature synthesis of strontium-doped lanthanum chromites

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10.1070/MC2000v010n04ABEH001290

Strontium-substituted lanthanum chromites ($La_{1-x}Sr_xCrO_3$) were prepared by self-propagating high-temperature synthesis (SHS) using solid oxidisers.

Strontium-doped lanthanum chromites are widely used as electrode materials in magneto-hydrodynamic generators and as an interconnect material in solid oxide fuel cells.[1,2] The material has been synthesised from a stoichiometric mixture of La_2O_3, Cr_2O_3 and $SrCO_3$ by conventional ceramic processes involving extensive heating, milling[3] and reheating. It has also been formed by glycino–nitrate[4] and citrate precipitation[5] processes. Unsubstituted lanthanum chromites have been prepared by self-propagating high-temperature synthesis (SHS) in an oxygen atmosphere and using solid oxidising agents such as sodium perchlorate.[6,7] These reactions proceed by means of a synthesis wave that moves through the reactant powders. The process is sufficiently exothermic to allow the ignition of successive layers of reactants. These syntheses include rapid reactions and minimal processing of the solids. In many cases, pure lanthanide chromite was formed directly in the reaction. Here, we report a synthesis of the strontium-substituted lanthanum chromites $La_{1-x}Sr_xCrO_3$ ($0 < x < 0.25$). In particular, we explored the effect of an internal oxidising agent on the reaction mixture. We investigated the reaction pathway using quenching techniques and thermogravimetry and differential thermal analysis (TGA/DTA).

Combustion processes were carried out in air with mechanically ground mixtures of La_2O_3, SrO_2, $SrCO_3$, Cr, CrO_3 and $NaClO_4$. All reagents were combined in stoichiometric quantities according to the reactions:

$$(1-x)/2\,La_2O_3 + x\,SrO_2 + Cr + y\,NaClO_4 \rightarrow La_{1-x}Sr_xCrO_3 + y\,NaCl \quad (1)$$

$$(1-x)/2\,La_2O_3 + x\,SrCO_3 + Cr + z\,NaClO_4 \rightarrow La_{1-x}Sr_xCrO_3 + z\,NaCl + x\,CO_2 \quad (2)$$

(x = 0, 0.16 or 0.25; y and z were adjusted to the oxygen stoichiometry)

This starting material (~10 g) was placed on a ceramic boat to form a line of powder of dimensions 1×5 cm. An electric filament on the upper surface of the sample was used to ignite the reactions. This promoted an orange propagation wave, which travelled at 2–5 mm s^{-1}. The reaction products were triturated with water to remove sodium chloride and analysed by X-ray powder diffraction, Raman spectroscopy, vibrating sample magnetometry and scanning electron microscopy/energy dispersive analysis by X-rays (SEM/EDAX). The reactions were studied by TGA/DTA on a SETARAM TAG24S24 instrument.

The SHS reaction is driven by the exothermic oxidation of chromium metal. Sodium perchlorate and strontium peroxide are internal oxidising agents in the reaction. Lanthanum oxide acts as a heat sink. In the strontium carbonate reaction, carbon dioxide is released. The maximum reaction temperature was 2170 K for the strontium carbonate reaction (2) and 2270 K for the strontium peroxide reaction (1). Chloride chemical analysis of the SHS product proves that more than 70% co-produced sodium chloride (formed by decomposition of the internal oxidising agent sodium perchlorate) is sublimed away from the product. The remaining sodium chloride is removed from the product to below detection limits simply by washing the product with water. The particle size of the washed products was in all cases around 50 μm. The specific surface areas of all the powders were in the range 3400–4000 $m^2\ kg^{-1}$. The EDAX spot analysis of the washed products showed the expected Sr:La:Cr ratios and notably no sodium or chlorine. Raman spectroscopy analysis (1 μm resolution) showed that the samples were homogeneous; an unsubstituted sample gave bands at 152, 177, 257, 439, 591 and 679 cm^{-1}. The introduction of strontium into lanthanum chromite causes additional bands to appear around 840 cm^{-1}.

The X-ray powder diffraction data for the SHS-prepared powders are consistent with that for materials prepared by conventional ceramic synthesis. The replacement of lanthanum by strontium in $La_{1-x}Sr_xCrO_3$ causes a reduction in the unit-cell

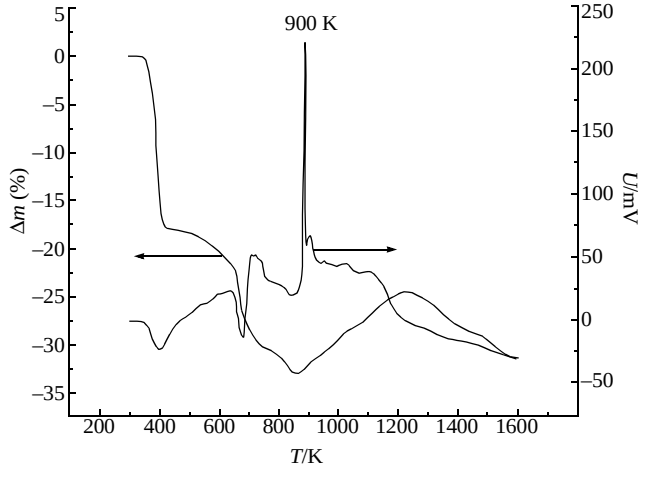

Figure 1 TGA and DTA curves for the SHS reaction $La_2O_3 + SrO_2 + Cr + NaClO_4$ under conditions of linear heating.

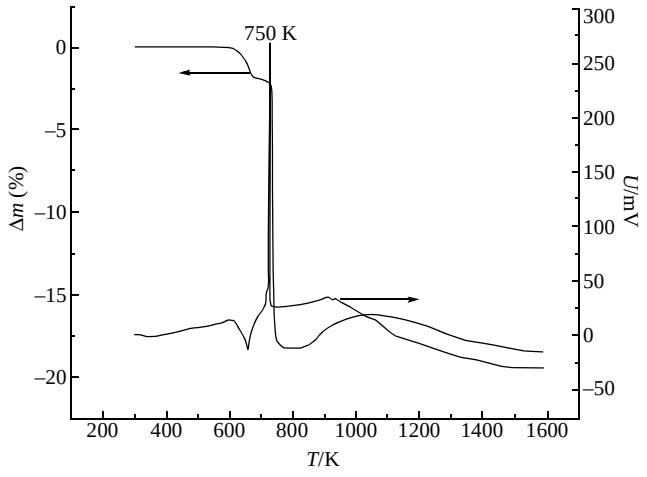

Figure 2 TGA and DTA curves for the SHS reaction $La_2O_3 + SrCO_3 + Cr + NaClO_4$ under conditions of linear heating.

Table 1 Structural and magnetic properties of $La_{1-x}Sr_xCrO_3$ compounds prepared by SHS (d is the picnometric density; σ is the specific saturation magnetization; V is the volume of a formula unit; a_0 is the pseudo-cubic parameter; EDAX compositions were determined to within 0.02).

x	Crystal lattice	Unit-cell parameters/nm	$V/10^{-2}$ nm^3	a_0 ($V^{1/3}$/nm)	$\sigma/10^{-3}$ A m^2 kg^{-1}	EDAX composition	$d/10^3$ kg m^{-3}
0	Orthorhombic	a = 0.5502 b = 0.5481 c = 0.7761	5.581	0.3882	0.106	$La_{1.01}Cr_{1.00}O_3$	6.50
0.16	Rhombohedral	a = 0.5462 (α = 60.260°)	5.794	0.3870	0.055	$La_{0.84}Sr_{0.15}CrO_3$	5.24
0.25	Rhombohedral	a = 0.5450 (α = 60.520°)	5.790	0.3869	0.031	$La_{0.75}Sr_{0.25}CrO_3$	5.04

volume (Table 1). The unsubstituted lanthanum chromite has an orthorhombic unit cell. The samples of $La_{0.84}Sr_{0.16}CrO_3$ and $La_{0.75}Sr_{0.25}CrO_3$ indexed with rhombohedral unit cells. The calculated pseudo-cubic parameter a_0 decreases with strontium substitution. This is related to a partial non-isovalent substitution of La^{3+} (ionic radius of 0.106 nm) from rare-earth sites of the perovskite-type structure by Sr^{2+} (ionic radius of 0.127 nm). The substitution of strontium in the structure partially oxidises the chromium to Cr^{4+} to maintain a charge balance. This oxidation of chromium causes a decrease in both the chromium–oxygen bond length and the unit-cell volume. As can be seen in Table 1, increasing strontium substitution leads to a reduction in the density and specific magnetisation. The reduction in magnetisation is caused by a change in the chromium-to-chromium interaction and can be correlated to the changes in the unit-cell structure.[3]

The reactions to form strontium-substituted lanthanum orthochromites were also studied using a 50:50 mix of CrO_3 and chromium metal. In this case, a drop in the synthesis temperature of 200 K was observed for both the strontium carbonate and strontium peroxide reactions. Chromium(VI) oxide acts both as a heat sink, reducing the exothermic effect of the reaction, and as an oxygen source to promote the fusion reaction:

$$CrO_3 + Cr \rightarrow Cr_2O_3. \quad (3)$$

The reaction mechanism was probed using liquid nitrogen to extinguish the reaction front and a large conical metal construction that inhibits the propagation wave as the neck of the cone decreases.[8] The level-by-level analysis of the frozen reaction zone by powder X-ray diffraction indicates that in both of the systems $LaCrO_3$, $LaCrO_4$ and SrO were formed as intermediates.

The reaction mechanism was also probed by extensive TGA/DTA measurements of all of the individual components over the temperature range 300–1800 K. Analysis of the chromium metal fuel source shows that it starts to oxidise under a flow of oxygen at 980 K and shows a maximum heat evolution at 1120 K. This oxidation corresponds to a weight increase by 13.3% and is incomplete.

$$2Cr + 1.5O_2 \rightarrow Cr_2O_3. \quad (4)$$

In the presence of La_2O_3 the oxidation of chromium metal occurs in a stepwise manner; the oxidation begins at 1150 K, and a maximum heat evolution is observed at 1270 K. The addition of an internal oxidant such as sodium perchlorate or strontium peroxide considerably modifies the chromium combustion process. As it is shown in Figure 1, in the reaction of chromium, lanthanum oxide, strontium peroxide and sodium perchlorate at temperatures higher than 393 K oxygen is partially released from SrO_2. In the range 393–668 K, a weight loss of 4.55% is observed, which was assigned to the partial decomposition of strontium peroxide

$$SrO_2 \rightarrow SrO_{1.28} + 0.36O_2. \quad (5)$$

The partial oxidation of chromium metal powder starts in the same time and temperature ranges. Further, with an increase in the temperature to 700–890 K, all strontium peroxide decomposes to form SrO. The decomposition of sodium perchlorate starts at 880 K

$$NaClO_4 \rightarrow NaClO_{2.5} + 0.75O_2. \quad (6)$$

As a result of the considerable release of oxygen accompanying the decomposition of sodium perchlorate and strontium peroxide, there is considerable oxidation of chromium, which together with the formation of SrO, promotes the formation of $SrCrO_4$.

$$2SrO + Cr_2O_3 + 1.5O_2 \rightarrow 2SrCrO_4. \quad (7)$$

The heat evolved in the reaction was maximum at 900 K (primarily from the oxidation of chromium metal); this promotes the reactions of chromium and lanthanum oxides

$$La_2O_3 + Cr_2O_3 \rightarrow 2LaCrO_3; \quad (8)$$

$$La_2O_3 + Cr_2O_3 + O_2 \rightarrow 2LaCrO_4. \quad (9)$$

The mutual dissolution of the intermediate reaction products happens in the temperature range 880–1120 K and is completed by the formation of the final product $La_{1-x}Sr_xCrO_3$ from the melt at 1260–1270 K.

The TGA/DTA curves for the reaction with $SrCO_3$ instead of SrO_2 are shown in Figure 2. The oxidation source in this reaction comes only from the decomposition of sodium perchlorate. The decomposition of sodium perchlorate is incremented with some oxygen released at 600–620 K, but the majority was released at 720–750 K. This second pulse of oxygen release corresponds to the maximium exotherm in the DTA. Note that in this system the intermediate $SrCrO_4$ is not formed. The temperature of CO_2 desorption from $SrCO_3$ with formation of SrO occurs at 990–1170 K. With a further increase in the temperature, SrO dissolved in the $LaCrO_3$–$LaCrO_4$ melt according to reactions (10) and (11) with subsequent crystallization of the final product from the melt.

$$(1-x)LaCrO_3 + xSrO + 0.5xCr_2O_3 \rightarrow La_{1-x}Sr_xCrO_3 + 0.25xO_2 \quad (10)$$

$$(1-x)LaCrO_4 + xSrO + 0.5xCr_2O_3 \rightarrow La_{1-x}Sr_xCrO_3 + 0.75xO_2 \quad (11)$$

SHS reactions offer a fast single-step route to the high-purity single-phase $La_{1-x}Sr_xCrO_3$. The reaction is promoted by the oxidation of chromium metal. The heat evolved in the reaction is sufficient to form a good solid solution without recourse to annealing of the product. The products from the SHS process show physical properties equivalent to those of conventionally prepared materials.[3–5] A number of important intermediates such as SrO, $SrCrO_4$, $LaCrO_3$, $LaCrO_4$ and Cr_2O_3 were isolated on the route to $La_{1-x}Sr_xCrO_3$.

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Received: 29th February 2000; Com. 00/1616