Journal of Optoelectronics and Advanced Materials Vol. 2, No. 5, 2000, p. 557-562

Section 3: Ceramic materials

WET-CHEMICAL METHODS FOR THE SYNTHESIS OF STRONTIUM DOPED $LaCrO_3$ CERAMIC POWDERS

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The paper deals with the preparation of $La_{1-x}Sr_xCrO_3$ (x = 0-0.2) from heteropolynuclear complex precursors isolated in the following systems: $Cr_2O_3{\cdot}xH_2O$ – $La(NO_3)_3$ – $Sr(NO_3)_2$ - A – NH_3 (A=CH_3COO^-, $C_2O_4^{2-}$). The complex precursors were characterised by chemical analysis, electronic and FT-IR spectra, as well as DTA-TG analysis. Doped lanthanum chromites were prepared by pyrolysis of corresponding complex precursors at 1000°C, 2-6h. The properties of doped lanthanum chromites were verified by XRD, unit cell volumes, FT-IR spectra, specific surface area measurements, as well as SEM-EDX analysis. According to the X-ray powder diffraction, all $La_{1-x}Sr_xCrO_{3-\delta}$ (x = 0 - 0.2) samples obtained from the corresponding acetate and oxalate precursors at 1000°C are single phase with orthorhombic perovskite like structure.

Keywords: Perovskite, Complex precursor, Lanthanum chromite

1. Introduction

High-temperature solid oxide fuel cells (SOFCs) have been extensively investigated for the last two decades because of their potential use as efficient power-generating devices. Alkaline earth metal-doped lanthanum chromites, $La_{1-x}M_xCrO_3$ (where M = Ca or Sr) are considered to be very promising materials for use as a separator or interconnecting materials in SOFCs. To be useful as an interconnect it is further required that material can be sintered to high density preferably at low temperature, and that the material is chemically and mechanically "compatible" with the other materials used in the SOFCs [1,2].

The electronic conductivity of the stoichiometric $LaCrO_3$ (ABO_3 perovskite structure) is increased by substitution with divalent ions on either the A- or B- sites. The most frequently used dopants are Ca and Sr on the A site or Mg, Cu or Ni on the B site. [3,4]

The substitution of a trivalent ion with a divalent one is electronically compensated by the formation of Cr^{4+} ions at high oxygen pressure, where the oxygen deficiency (δ) has been found close to zero. At low oxygen pressure, doped lanthanum chromites loose oxygen and oxygen vacancies are formed [5].

The paper deals with the preparation of $La_{1-x}Sr_xCrO_3$ (x = 0-0.3) from heteropolynuclear complex precursors isolated in the following systems: $Cr_2O_3{\cdot}xH_2O$ – $La(NO_3)_3$ – $Sr(NO_3)_2$ -A – NH_3 (A = CH_3COO^-, $C_2O_4^{2-}$).

2. Experimental

The synthesis procedure proposed in this paper includes three stages: *(i)* fresh $Cr_2O_3{\cdot}xH_2O$ preparation from a waste acetic solution with high chromium content (24.1%), *(ii)* synthesis of complex precursors by acetate or oxalate methods and *(iii)* synthesis of strontium doped lanthanum chromite by calcining of isolated complex precursors.

The waste acetic solution with high chromium content is obtained from purification equipment for technical acetic acid, in which CrO_3 is used as catalyst for the oxidation of acetaldehyde to acetic acid. [6]

Acetate method. A mixture of freshly prepared $Cr_2O_3 \cdot xH_2O$, $La(CH_3COO)_3$ and $Sr(CH_3COO)_2$ in aqueous solution (molar ratio La:Cr:Sr = (1-x):1: x, where x = 0 - 0.2 was treated with glacial acetic acid up to $Cr_2O_3 \cdot xH_2O$ dissolution. This solution was precipitated with 10% ammonia solution at *p*H=7.5. After 2h of refluxing time, the complex precursors were filtered off, washed with ether and dried in air.

Oxalate method. The starting materials were: freshly prepared $Cr_2O_3 \cdot xH_2O$, aqueous solutions of $La(NO_3)_3$ and $Sr(NO_3)_2$ in molar ratio La:Cr:Sr = (1-x):1: x (x = 0-0.2). A mixture of these materials was treated with 5% aqueous solution of $H_2C_2O_4$ and then neutralised with 10% ammonia to *p*H=7. After refluxing (2h) the insoluble oxalate precursors were filtered off, washed with ether and dried in air.

Strontium doped lanthanum chromites were prepared by pyrolysis of heteropolynuclear complex precursors at 1000°C for 2-6 h.

The complex precursors were characterised by chemical analysis (AAS), electronic and FT-IR spectra, as well as DTA-TG analysis. The properties of doped lanthanum chromites were verified by XRD, unit cell volumes, specific surface area measurements, as well as SEM-EDX analysis. Specific surface area of chromites was determined by B.E.T. method using nitrogen as the adsorbate.

3. Results and discussion

Precursor characterization

The *electronic reflection spectra* of the $La_{1-x}Sr_xCrO_3$ precursors (fig.1) presents two characteristic bands for the Cr(III) (d^3) ion in a distorted octahedral geometry (one at 420 nm assigned to ${}^4T_{1g} \leftarrow {}^4A_{2g}$ and another one at 570 nm assigned to ${}^4T_{2g} \leftarrow {}^4A_{2g}$).[7]

The *FT-IR spectra* (fig. 2) of acetate precursors are very similar, the bands corresponding to stretching vibration frequency of bidentate bridging CH_3COO^- ion (1456.2 cm^{-1}, 1559.1 cm^{-1}, 1620.6 cm^{-1}) of coordinated H_2O ($\nu_{s,as(OH)}$=3390 cm^{-1}, δ_{HOH}=1620 cm^{-1}, ρ_{HOH}=650-670 cm^{-1}) and hydroxyl groups (ν_{MOH}=940 cm^{-1}, 1030 cm^{-1}) being present [8].

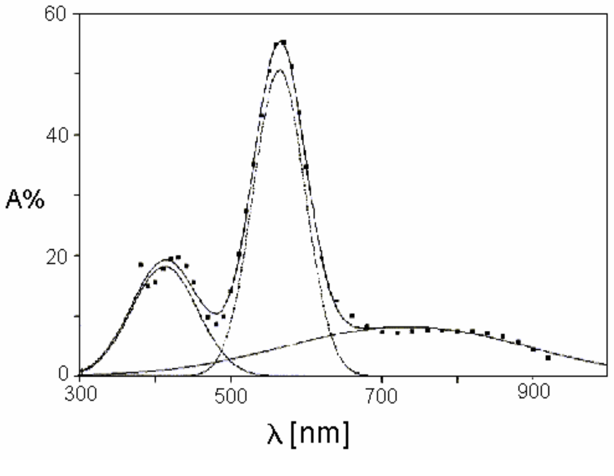

Fig. 1. Electronic spectrum of $[La_{0.9}Sr_{0.1}Cr(C_2O_4)_2(OH)_2(H_2O)_4]\cdot H_2O$.

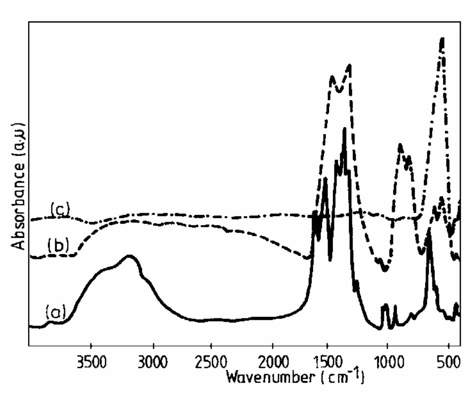

Fig. 2. FT-IR spectra of $La_{0.9}Sr_{0.1}CrO_3$ precursor (a. 25°C; b. 370°C; c. 1000°C).

The thermal decomposition in steps of the complex acetate was correlated with the results of the FT-IR spectral data. The frequencies of bidentate CH_3COO^- ion and coordinated H_2O disappear in acetate precursors calcinated at 370°C and only the vibration modes of monodentate CH_3COO^- remain.

In the FT-IR spectra of oxalate precursors, beside the coordinated H_2O bands, vibration modes of the oxalate group are present ($\nu_{as\ OCO}$=1640 cm^{-1}, $\nu_{s\ OCO}$=1360, 1320 cm^{-1}, δ_{OCO}=825 cm^{-1}). The positions of these bands support the tetradentate coordination of oxalate anions in their planar structure [9].

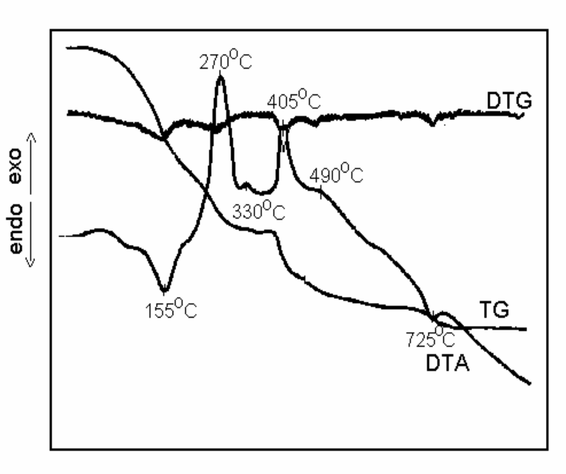

Fig. 3. DTA-TG curve of $La_{0.9}Sr_{0.1}CrO_3$ oxalate based precursor.

The thermal decomposition of acetate and oxalate precursors was studied in order to establish the best conditions for $La_{1-x}Sr_xCrO_3$ synthesis. The DTA-TG curve of $[La_{0.9}Sr_{0.1}Cr(C_2O_4)_3(H_2O)_4]\cdot 4H_2O$ present two endothermic effects (90°C and 155°C) assigned to hydration and coordinated water loss and 5 exothermic effects assigned to the decomposition of organic ligand (26.2% loss) with the formation of oxalato-carbonate, carbonate and finally $La_{1-x}Sr_xCrO_3$ lattice. It is noticed that in 725°-820°C temperature range, the DTA-TG curve show a small endothermic effects with 3% loss that could be assigned to the loss of OH groups adsorbed on the surface of the powder and decomposition of $SrCO_3$ with the formation of $La_{1-x}Sr_xCrO_3$.

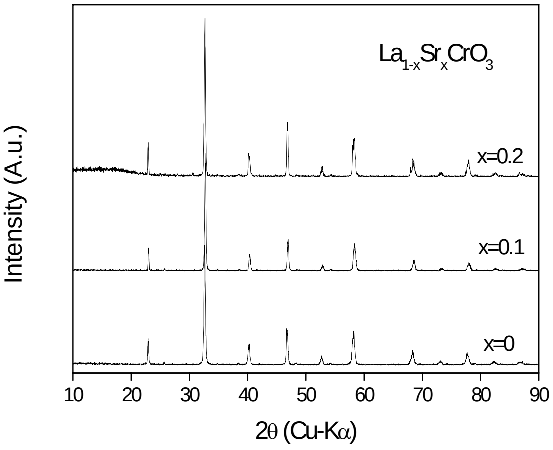

Fig. 4. XRD spectra of $La_{1-x}Sr_xCrO_3$ obtained from acetate-based precursors at 800°C, 0.5h for $LaCrO_3$,1000°C and 2h for (x=0.1-0.2).

$La_{1-x}Sr_xCrO_3$ powders characterization

According to the *X-ray powder diffraction,* all $La_{1-x}Sr_xCrO_{3-\delta}$ (x=0-0.2) samples obtained from the corresponding acetate and oxalate precursors at 1000°C are single phase with orthorhombic perovskite like structure. The unit cell volume of $La_{1-x}Sr_xCrO_3$ decreases with the increasing of Sr^{2+} content as a result of La^{3+} replacement ($r_{La^{3+}} = 1.15$ Å) with Sr^{2+} ($r_{Sr^{2+}} = 1.13$ Å). The FT-IR spectra of the precursors (thermal decomposed at 800°C, 2h) with a composition up to x = 0.2 is very similar to that of pure lanthanum chromite. For x = 0.3, the FT-IR spectra show significant differences (the absence of O-Cr-O bending vibration, the broadening of the bands and the appearance of CrO_4^{2-} characteristic vibration modes. This last frequencies disappear by thermal treatment of all type of precursors at 1000°C, 2h, as XRD patterns confirm.

Table 1. Some properties of pure and strontium doped lanthanum chromite samples.

Sample	*Precursor type*	*Preparation conditions*	*V [Å^3]*	*S [m^2/g]*
$LaCrO_3$	Oxalate	800, 0.5h	234.85	3.45
$La_{0.9}Sr_{0.1}CrO_3$	Oxalate	800, 6h	233.48	4.25
$La_{0.9}Sr_{0.1}CrO_3$	Oxalate	900, 2h	234.95	3.26
$La_{0.9}Sr_{0.1}CrO_3$	Oxalate	1000, 2h	233.52	3.08
$La_{0.8}Sr_{0.2}CrO_3$	Oxalate	1000, 2h	232.41	2.45
$LaCrO_3$	Acetate	800, 0.5h	233.95	0.95
$La_{0.9}Sr_{0.1}CrO_3$	Acetate	900, 2h	233.30	2.89
$La_{0.8}Sr_{0.2}CrO_3$	Acetate	1000, 2h	232.65	4.60

SEM examination of the $La_{1-x}Sr_xCrO_{3-\delta}$ samples calcinated at 1000°C, 2h, showed porosity. All samples of strontium-doped lanthanum chromites obtained from acetate and oxalate type precursors have micronic particles with tendency of forming of agglomerates.

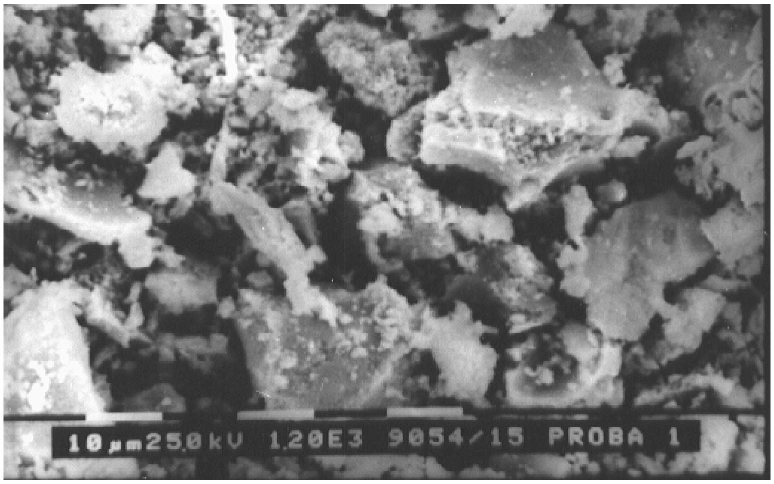

Fig. 5. Scanning electronic micrograph of $La_{0.9}Sr_{0.1}CrO_3$ obtained from acetate-type precursor at 1000°C.

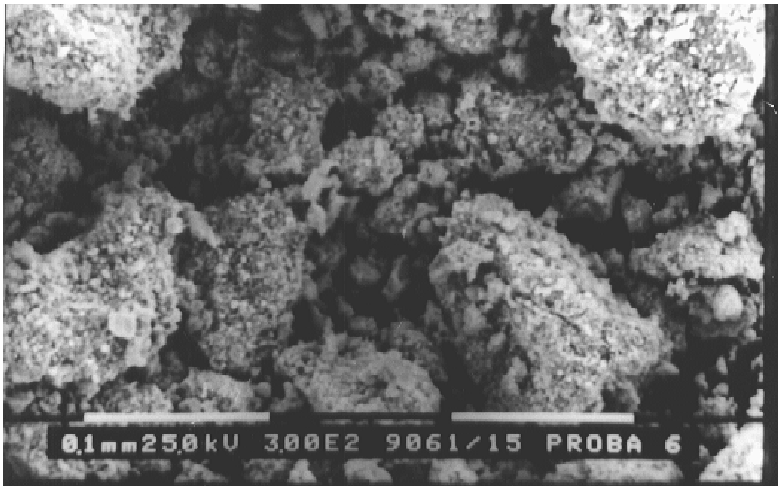

Fig. 6. Scanning electronic micrograph of $La_{0.9}Sr_{0.1}CrO_3$ obtained from oxalate-type precursor at 1000°C.

4. Conclusions

Strontium-doped lanthanum chromites, $La_{1-x}Sr_xCrO_3$ (x = 0 - 0.2) were obtained by calcining of some new heteropolinuclear complex precursors isolated in the following systems: $Cr_2O_3 \cdot xH_2O$ - $La(NO_3)_3$ – $Sr(NO_3)_2$ – A – NH_3 (A = $C_2O_4^{2-}$, CH_3COO^-). The complex precursors were characterised by chemical analysis, electronic and FT-IR spectra, as well as DTA-TG analysis.

$La_{1-x}Sr_xCrO_3$ samples were investigated by XRD, FT-IR spectra, SEM-EDX analysis, as well as specific surface area measurements. The unit cell volume values decreased with x increasing sustaining the partial replacement of La^{3+} ions with Sr^{2+} cations of smaller ionic radius.

The specific surface area of doped lanthanum chromites obtained by calcining of oxalate precursors was generally bigger than that of chromites obtained from acetate precursors. Strontium-doped lanthanum chromites powders obtained from acetate and oxalate type precursors have micronic particles with tendency of forming of agglomerates.

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