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Lanthanum chromites doped with divalent transition metals

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Abstract

Heteropolynuclear complex compounds isolated in $Cr_2O_3{\cdot}xH_2O$–$La(NO_3)_3$–$M(NO_3)_2$–A–NH_3, (A = CH_3COO^-,$C_2O_4^{2-}$; M = Cu, Ni) systems were used as precursors for $LaCr_{1-x}M_xO_3$. The perovskite structure of doped lanthanum chromites was determined by XRD analysis. The unit cell volumes, specific surface areas and magnetic properties were investigated. The proposed methods offer new, simple, less expensive procedures for obtaining doped lanthanum chromites. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

The perovskite lanthanum chromite and especially doped $LaCrO_3$ has recently received much interest as high-temperature electrode materials and solid oxide fuel cell interconnects [1–5].

Many authors indicated that both the sinterability and the electrical conductivity of $LaCrO_3$ could be improved by the substitution of a lower-valent ion such as Cu^{2+} or Mg^{2+} at the Cr^{3+} site or of Sr^{2+} at the La^{3+} site [6–9]. As a result formation of oxygen vacancies and/or Cr^{4+} ions will be enhanced to preserve electroneutrality with cation stoichiometry; this, in turn will influence the electrical properties. But all these changes depend on the preparation methods of these perovskite ceramics (nature of reagents used in the synthesis, sintering temperature, oxygen pressure, etc.).

Preparation of mixed oxides by thermal decomposition of heteropolynuclear complex precursors represents an important area of research; the advantages of such a method are improved quality of the final mixed oxides (high purity and homogeneity) with low cost of precursors.

In this paper we report on pure and doped lanthanum chromite synthesis from complex compounds precursors isolated in $Cr_2O_3{\cdot}xH_2O$–$La(NO_3)_3$–$M(NO_3)_2$–A–NH_3 (M = Ni, Cu, A = CH_3COO^-, $C_2O_4^{2-}$) systems.

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 pure or doped lanthanum chromite by thermal treatment of 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.

2.1. Acetate method

A mixture of freshly prepared $Cr_2O_3{\cdot}xH_2O$ [10], $La(CH_3COO)_3$ and $M(CH_3COO)_2$ (M = Ni or Cu) in aqueous solution (molar ratio La:Cr:M(II) = 1:(1−x):x, where x = 0.1–0.5 was treated with glacial acetic acid up to $Cr_2O_3{\cdot}xH_2O$ dissolution. This solution was precipitated with 10% ammonia solution at pH 7.5. After 2 h of refluxing time, the complex precursors were filtered off, washed with ether and dried in air.

2.2. Oxalate method

The starting materials were: freshly prepared $Cr_2O_3{\cdot}xH_2O$, aqueous solutions of $La(NO_3)_3$ and $M(NO_3)_2$ in molar ratio La:Cr:M(II) = 1:(1−x):x

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(M(II) = Ni or Cu and $x = 0.1$–0.5). A mixture of these materials was treated with 5% aqueous solution of $H_2C_2O_4$ and then neutralised with 10% ammonia to pH 7. After refluxing (2 h) the insoluble oxalate precursors were filtered off, washed with ether and dried in air.

In both methods, pure $LaCrO_3$ was obtained by calcination of heteropolynuclear complex compounds at 800°C, 30 min. Doped lanthanum chromites, $LaCr_{1-x}M_xO_3$ (M = Ni, Cu, $x = 0.1$–0.5) were prepared by pyrolysis of complex precursors at 900, 1000°C, 2 h.

Precursors were characterized by chemical analysis (AAS), electronic and FT–IR spectra, as well as DTA–TG analysis.

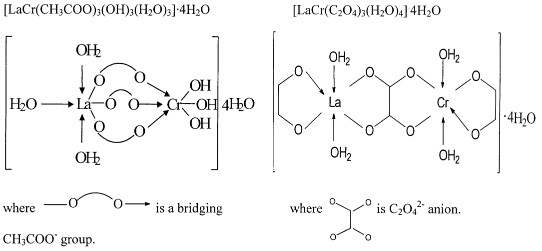
3. Results and discussion

3.1. Precursors characterization

The electronic reflection spectrum of $LaCrO_3$ precursors presents two characteristic bands for 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 ${}^4T_{2g} \leftarrow {}^4A_{2g}$. In the electronic spectra of all $LaCr_{1-x}Ni_xO_3$ complex precursors, beside the Cr(III) octahedral bands, two other bands, at 370 and 660 nm, appear: these were assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and respectively ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transitions for Ni(II) (d^8) ion in an octahedral field. In all electronic spectra of La–Cr–Cu complex precursors, the 570 nm band of Cr(III) in octahedral field is overlapped by an asymmetrical broad band (600–800 nm) characteristic for Cu(II) (d^9) ion in a distorted octahedral geometry (Jahn Teller effect) [11].

The FT–IR spectra (Fig. 1) of acetate precursors are very similar, the bands corresponding to stretching vibration frequency of bidentate bridging CH_3COO^- ion (1456.2; 1559.1, 1620.6 cm^{-1}) of coordinated H_2O ($\nu_{s,as,OH} = 3390$ cm^{-1}, $\delta_{HOH} = 1620$ cm^{-1}, $\rho_{HOH} = 650$–670 cm^{-1}) and hydroxyl groups ($\nu_{MOH} = 940$, 1030 cm^{-1}) are present.

The FT–IR spectra (Fig. 2) of oxalate precursors reveal the coordinated H_2O bands and vibration modes of the oxalate group ($\nu_{asOCO} = 1640$ cm^{-1}, $\nu_{sOCO} = 1360$, 1320 cm^{-1}, $\delta_{OCO} = 825$ cm^{-1}). The positions of these bands support the tetradentate coordination of oxalate anions in a planar structure [12]. The chemical and spectral data presented above, support the following structural formula for La–Cr-acetate and La–Cr-oxalate precursors:



The thermal decomposition of La–Cr-acetate and La–Cr-oxalate precursors was studied in order to establish the best conditions for pure $LaCrO_3$ synthesis. The DTA–TG curves of acetate precursor [Fig. 3(a)] show two endothermic effects, assigned to hydration water loss (60–110°C), to precursor decomposition with the loss of coordination water (160–280°C) and a very strong exothermic effect (380°C) assigned to the combustion of the organic ligand and crystallization with $LaCrO_3$ formation (400–750°C).

Oxalate precursors also decompose in steps [Fig. 3(b)] with the formation of oxalato-carbonate, carbonate and finally (750–770°C) $LaCrO_3$ lattice (probably with oxygen deficiency). In both cases (acetate and oxalate precursors) the experimental total weight loss is higher than theoretical and could be due to vaporization of chromium.

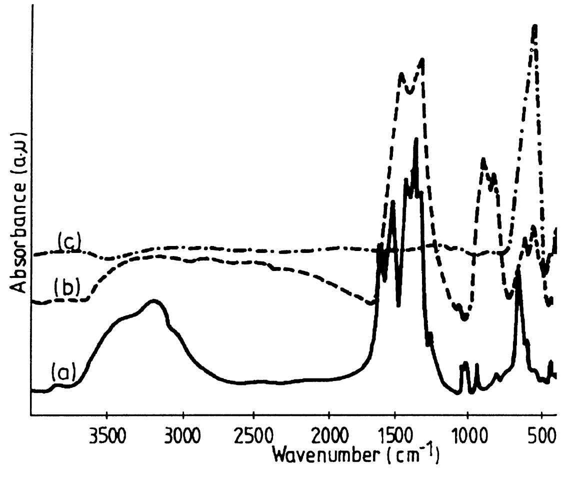


Fig. 1. FT–IR spectra of $[LaCr(CH_3COO)_3(OH)_3(H_2O)_3]\cdot 4H_2O$: (a) 25°C; (b) 370°C; (c) 800°C.

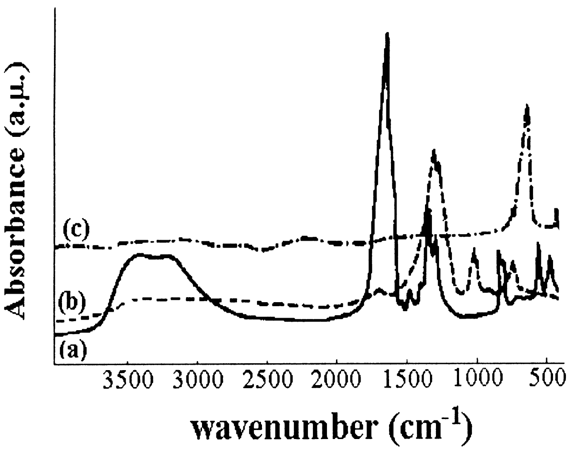


Fig. 2. FT–IR spectra of $[LaCr(C_2O_4)_3(H_2O)_4]\cdot 4H_2O$: (a) 25°C; (b) 550°C; (c) 800°C.

Thermal decomposition in steps of La–Cr-acetate or La–Cr-oxalate precursors is also supported by FT-IR spectra [see Figs. 1(b) and 2(b)]. In the spectrum of acetate precursor calcined at 370°C, the frequencies of bidentate CH_3COO^- ion and coordinated H_2O disappear and only $\delta_{\text{M-OH}}$ and ν_{asOCO} (monodentate CH_3COO^- ion) frequencies remain. In the spectrum of oxalate precursor decomposed at 550°C, the frequencies of oxalate (band ν_{asOCO}) disappear and other two bands (at 1030 and 710 cm^{-1}) characteristic for CO_3^{2-} ion are present. The spectra of precursors calcinated at 800°C present only the characteristic bands for $LaCrO_3$ [Figs. 1(c) and 2(c)], namely strong bands around 600 and 425 cm^{-1} corresponding to the stretching vibration of the Cr–O and O–Cr–O bonds.

3.2. *Pure $LaCrO_3$ and $LaCr_{1-x}M_xO_3$ (M = Ni, Cu) characterization*

According to the X-ray powder diffraction patterns, $LaCrO_3$ and $LaCr_{1-x}M_xO_3$ obtained in this paper are single phase with orthorhombic perovskite-like structure. The unit cell volume and the specific surface area of $LaCr_{1-x}M_xO_3$ increase with x content (Figs. 4 and

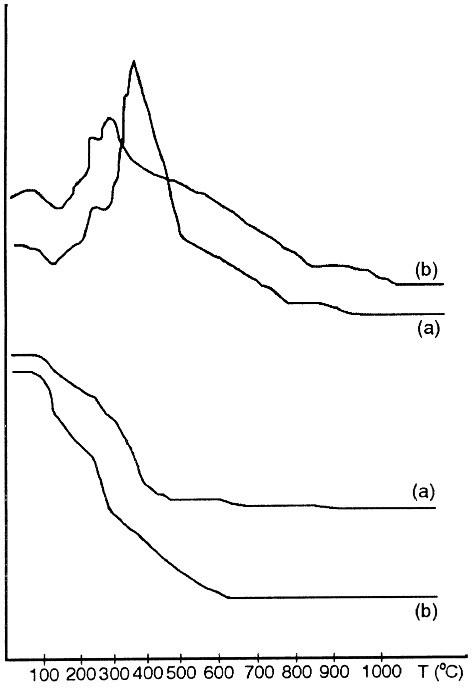


Fig. 3. DTA–TG curves of complex precursors: (a) La–Cr-acetate and (b) La–Cr-oxalate.

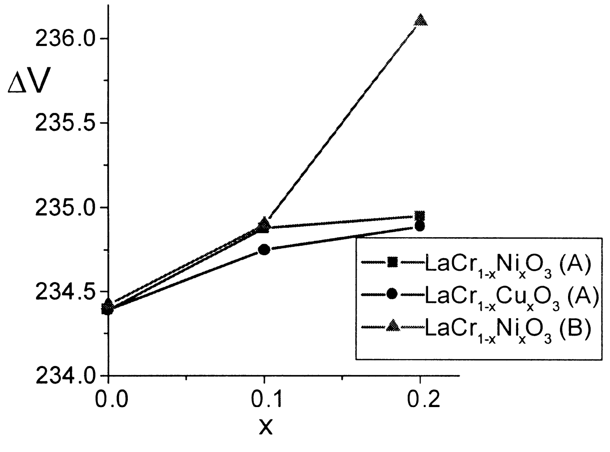


Fig. 4. Unit cell volume of $LaCr_{1-x}M_xO_3$: (A) from acetate precursors; (B) from oxalate precursors.

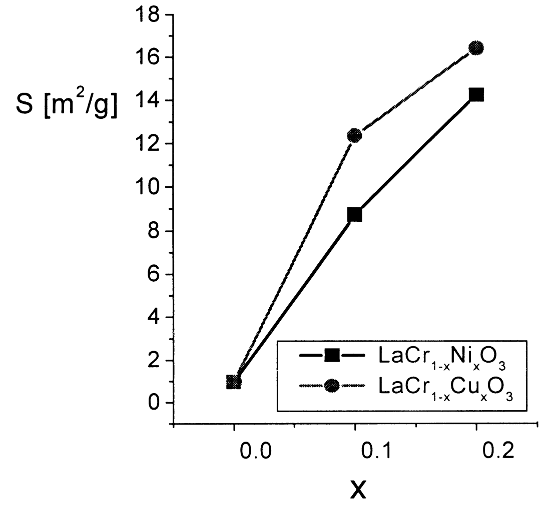


Fig. 5. Specific surface area of $LaCr_{1-x}M_xO_3$ (from acetate precursors).

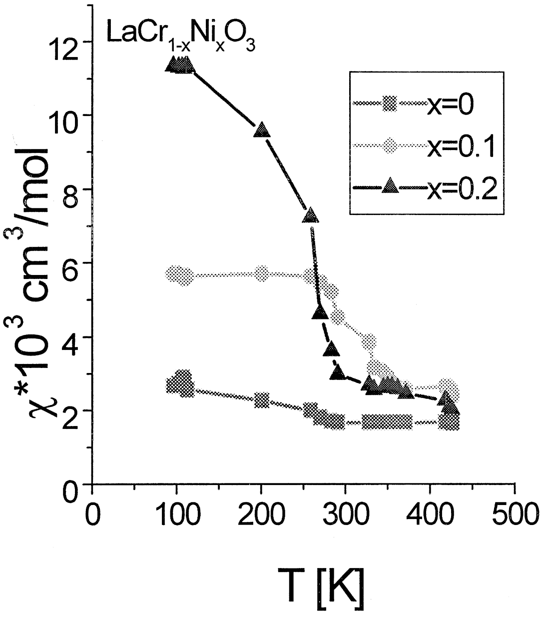


Fig. 6. Magnetic susceptibilities vs temperature for $LaCr_{1-x}Ni_xO_3$.

5). This result implied that Cr^{3+} ions are replaced by divalent cations with larger ionic radii cations (Ni^{2+} 0.70 Å, Cu^{2+} 0.73 Å) than that of Cr^{3+} (0.615 Å).

For characterization of $LaCr_{1-x}M_xO_3$ oxide species, magnetic data were also determined. Fig. 6 shows the temperature dependence of magnetic susceptibilities for $LaCr_{1-x}Ni_xO_3$ obtained from acetate precursors at 1000°C. For all samples studied the magnetic susceptibility in the paramagnetic range decreases and the Néel temperature becomes lower as x increases. The increased distance between Cr^{3+} (as the unit cell size increases) might be responsible for the reduction of the Néel temperature.

4. Conclusions

Doped lanthanum chromites with the formula $LaCr_{1-x}M_xO_3$ ($M = Ni, Cu$; $x = 0.1–0.5$) were obtained by calcination of some new heteropolynuclear complex precursors isolated in the $Cr_2O_3 \cdot xH_2O–La(NO_3)_3–M(NO_3)_2–A–NH_3$, ($A = CH_3COO^-$, $C_2O_4^{2-}$ $M = Cu, Ni$) systems. In all cases the calcination temperature of precursors prepared in acetate systems was lower than that for precursors obtained in oxalate systems. At $x = 0.5$ a good orthorhombic perovskite phase was obtained only in the case of Ni^{2+} but a new phase, $La_2CrMO_{5+\delta}$, was identified by doping with Cu^{2+} [8]. The unit cell volume of $LaCr_{1-x}M_xO_3$ ($x = 0–0.2$) oxides monotonically increased with x increasing sustaining the partial replace of Cr^{3+} ions with cations of larger radii.

The specific surface area of the doped lanthanum chromites obtained by calcination of oxalate precursors was generally greater than that of chromites obtained from acetate precursors. The magnetic susceptibilities of $LaCr_{1-x}Ni_xO_3$ oxides decrease with increasing x content.

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