



# Bulk and surface structure characterization of nanoscopic silver doped lanthanum chromites

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## ABSTRACT

Crystalline state of lanthanum chromites with silver as a dopant has been studied by X-ray diffraction and transmission electron microscopy reveals microscopic properties of grain boundaries. X-ray photoelectron spectroscopy has been used to analyze surface states with atomic ratio of La, Cr, O and Ag as a dopant.  $\text{LaCrO}_3$  shows mixed valence states of chromium while the silver doped samples exhibit differences in chromium concentration with the oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  in presence of chromium nitrate as a precursor salt. Trivalent stable state of chromium is observed for samples synthesized by chromic acetate as a precursor salt.

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## 1. Introduction

Among various perovskite materials lanthanum chromite has been found to be very promising due to its higher surface acidity favorable for catalytic reactions especially liquid phase esterification [1]. Literature on this material have been focused on partial substitution of perovskite lattice oxide by metal ions such as alkaline earth metal i.e. calcium enhances density and phase purity of the sample together with increasing  $\text{Cr}^{6+}$  content of chromium ions that leads to an increase in electrical conductivity [2]. Cobalt substituted lanthanum chromite exhibits increase in vacancy, ordering and compositional variation in redox properties of surface [3]. Silver doped lanthanum cobaltite as a monolithic catalyst enhances activity (i.e. mobility of lattice oxygen) in the combustion of methane [4]. Higher concentration of silver doping in lanthanum ferrite enhances the ratio of mixed valency that is favorable for SOFC and photo catalytic applications [5]. Silver is a widely applicable dopant due to its limited solubility with site occupancy in a dispersed as well as dopant form. Depending on the nature of the transition metal, silver as a substituent leads to partial reduction of transition metal ions and enhances mobility of

oxygen (i.e. creation of oxygen vacancies) in a perovskite lattice. Advances in the field referred to above requires X-ray photoelectron spectroscopic studies for better understanding of the valence states of ions in the perovskite lattice both bulk and surface.

Siegbahn et al. has already explained the role of ESCA technique in the study of free molecules [6,7]. Multiplet splitting of chromium complexes and effect of covalency related to stability of oxidation states has been reported by Nefedov and Briggs and Seah [8,9]. From the XPS studies, Frost et al. has reported the role of unpaired electron in open shell transition metal complexes and the degree of spin delocalization in the valence orbitals [10]. Cox and Muller et al. have studied the band intensities in the photoelectron spectra of open shell molecules and critical exponents at structural phase transitions [11,12]. Cerium and strontium doped lanthanum manganites have also been studied by XPS technique and they show changes in the spectral shapes as a function of cerium content and also influence the bond strengths without changing the parent lattice [13]. Strontium doped lanthanum manganite is a substitute for cathode material in solid oxide fuel cell and strontium rich phase and surface manganese ions are the active sites for oxygen reactions [14].

The present work reports the X-ray photoelectron studies of lanthanum chromite and silver doped lanthanum chromite nanoparticles synthesized by microwave combustion method. The influence of silver as a dopant at A (La) and B (Cr) site, role of precursor salts (chromium nitrate and chromic acetate), oxidation state,

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surface atomic ratio of constituent elements and existing state have been studied by energy dispersive analysis of X-rays.

## 2. Experimental

All the chemicals used were of AR grade. Lanthanum nitrate, chromium nitrate, chromic acetate and urea were obtained from Loba Chemie, while silver nitrate was from Qualigens. Lanthanum chromite and silver doped lanthanum chromite were synthesized by microwave activation method. Syntheses were carried out by varying precursor salts of chromium. During synthesis, the precursor salts were mixed in stoichiometric ratios and subjected to microwave activation at 0.56 kW power. Details of the experimental procedure are given elsewhere [15]. X-ray diffraction analysis of the powders were carried out on a Bruker AXSD-8 Advance X-ray diffractometer with monochromatic  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Silicon was used as an external standard for correction due to instrumental broadening. Diffraction data were collected from  $20^\circ$  to  $80^\circ$  at a scan rate of  $0.1^\circ \text{ min}^{-1}$ . Transmission electron micrographs (TEM) of the samples were observed under the Philips CM-200 instrument at an accelerating voltage of 200 kV. Suspensions of the samples in isopropanol were well dispersed and loaded on carbon coated grids of 200 mesh size. The grids were then dried under IR lamp and viewed under the microscope. XPS measurements were performed on a V.G. Microtech Unit ESCA 3000 Spectrometer with twin anode ( $\text{MgK}\alpha$  1253.6 eV). The vacuum in the analyzing chamber was  $<1 \times 10^{-9}$  Torr. Multichannel detectors were used to detect the photoelectrons and a spherical sector analyzer was used to detect the energies of photoelectrons. The X-ray flux was 200 W. The spectrometer was calibrated by determining the binding energy values of La, Cr, O, and Ag using spectroscopically pure metals obtained from Johnson-Matthey, London. The binding energy values (measured to an accuracy of 0.2 eV) are in good agreement with the literature values. The XPS spectra were acquired at 50 eV pass energy, 5 mm slit width and take off angle (angle between electron emission direction and surface plane) of  $50^\circ$ . Due to a large number of channeltrons the detection limit had been increased. The instrumental resolution under these conditions was 1.6 eV full width at half maximum (FWHM) for the Au 4f level. The sample was mounted as a thin layer film on the sample holder and used for recording the XPS spectra. All the spectra were recorded with similar spectrometric parameters. The general scan and C 1s, O 1s, La, Cr, and Ag 3d core levels were recorded with reference as un-monochromatized  $\text{MgK}\alpha$  (1253.6 eV) radiation at 50 eV pass energy and take off angle ( $55^\circ$ ). The peak shift due to charging was corrected using the C 1s level at 284.6 eV as an internal standard.

Energy dispersive analysis of X-rays (EDAX) was taken on an analytical instrument (JEOL JSM 6360A). The data were recorded by coating the films of the samples with Ag–Pd alloy using vapor deposition technique.

## 3. Results and discussion

Fig. 1 shows the X-ray diffractograms of both,  $\text{LaCrO}_3$  and silver doped  $\text{LaCrO}_3$  samples synthesized at 0.56 kW microwave power using chromium nitrate and chromic acetate as precursor salts and urea as a fuel. Fig. 1a and b depicts the X-ray diffractograms of  $\text{LaCrO}_3$  samples with characteristic peaks at  $2\theta$  values of  $32.3^\circ$ ,  $39.9^\circ$ ,  $46.4^\circ$ ,  $67.8^\circ$  and  $77.1^\circ$  attributable to (110), (021), (202), (220), and (312) planes of a hexagonal lattice (JCPDS no. 33-0702). The diffractograms of silver doped  $\text{LaCrO}_3$  samples (Fig. 1c–f) exhibit additional peaks corresponding to metallic silver at  $2\theta$  values of  $38.3^\circ$ ,  $44.1^\circ$  and  $64.4^\circ$ . The data has been correlated with JCPDS pattern (04-783).

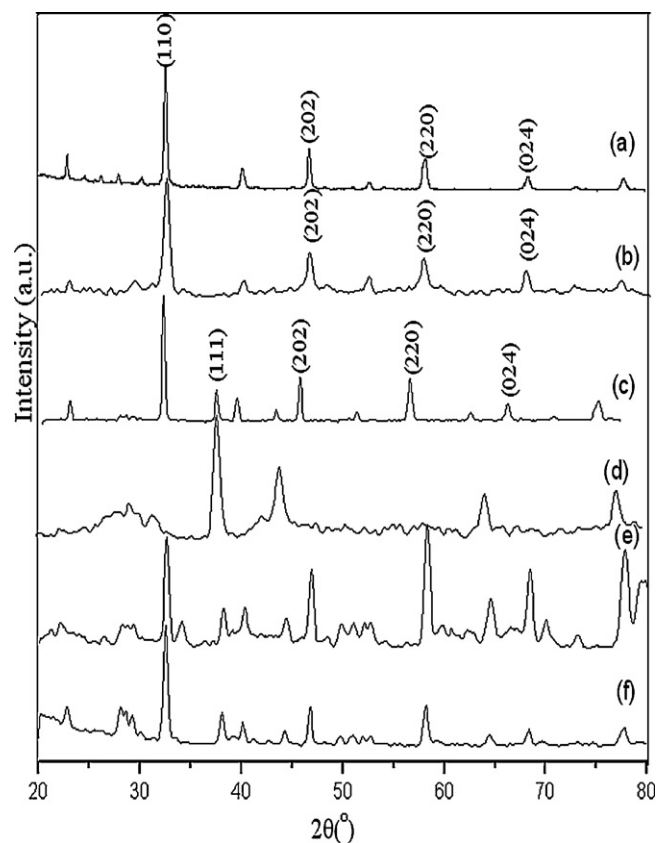


Fig. 1. X-ray diffractograms of (a)  $\text{LaCrO}_{3+\delta}$ , (c)  $\text{La}_{0.75}\text{Ag}_{0.25}\text{CrO}_{3+\delta}$ , (e)  $\text{LaCr}_{0.75}\text{Ag}_{0.25}\text{O}_{3+\delta}$  CN as a precursor salt. (b)  $\text{LaCrO}_{3+\delta}$ , (d)  $\text{La}_{0.75}\text{Ag}_{0.25}\text{CrO}_{3+\delta}$  and (f)  $\text{LaCr}_{0.75}\text{Ag}_{0.25}\text{O}_{3+\delta}$  CA as a precursor salt.

The theoretical densities, cell volume and crystallite size of the particles calculated from the XRD data for each sample are given in Table 1 and (CN) is designated for chromium nitrate precursor salt and (CA) for chromic acetate precursor salt. A comparison of the data in Table 1 reveals significant differences in lattice parameters in case of silver doped samples. The doped samples synthesized by using chromium nitrate as a precursor salt exhibit lattice expansion, while, those prepared by using chromic acetate show contraction in cell volume. This can be attributed to the mismatch of ionic radii and co-ordination number (i.e. dodecahedron and polyhedron). The differences in the theoretical densities can be accounted in terms of variation in the unit cell volume, molar mass of compounds and A and B site deficiencies in the crystal lattice. Further, the crystallite sizes of doped samples are observed to be lower compared to pure  $\text{LaCrO}_3$ .

The transmission electron micrographs (TEM) of the samples are shown in Fig. 2. As observed from the micrographs (Fig. 2a and b),  $\text{LaCrO}_3$  particles are irregular in shape with a particle size distribution  $\sim 20$ – $100$  nm and  $\sim 30$ – $100$  nm respectively. The silver doped samples (both A (La) and B (Cr) site) exhibit particles with significantly smaller size (Table 1) and spherical morphology (Fig. 2c–f).

Further, the surface compositions in terms of atomic concentration ratios of all the samples were established from the XPS analysis, considering the peak areas and sensitivity factor. The general survey scans (not included) showed electronic levels of La (800–855 eV), Cr (570–585 eV) and O (525–533 eV) atoms for all the samples and additional peak corresponding to silver atoms (360–380 eV) for doped samples. The binding energy data of the respective elements is included in Table 2.

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