

Silver doped lanthanum chromites by microwave combustion method

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Abstract

Considering the advantages of microwave combustion technique with the possibility of utilizing cheap precursors, short reaction time and nanocrystalline products, the present work reports the synthesis of silver doped lanthanum chromites. Structural and physicochemical properties were investigated with the help of various characterization techniques. The FTIR spectrum reveals the characteristic metal oxygen bands for Cr–O stretching at 604 cm^{-1} , O–Cr–O bending mode at 419 cm^{-1} and Ag–O bands at 561 cm^{-1} and 443 cm^{-1} . The powder X-ray diffraction patterns exhibit the formation of hexagonal structure with the dopant peaks at 2θ values of 38.3° , 44.1° and 64.4° apart from the peaks corresponding to lanthanum chromite. TGA analysis of the samples shows stable behavior of the product. Nanosized particles with size as small as $\sim 7\text{--}8\text{ nm}$ and larger ones $\sim 20\text{--}26\text{ nm}$ are observed from transmission electron micrographs. Room temperature magnetic study exhibits hysteresis loop formation during magnetization of samples.

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1. Introduction

Lanthanum based perovskites (ABO_3) find interesting applications such as thermal indicators and barriers [1,2], interconnect materials for SOFCs [3], ionic conductors [4] and photocatalysts [5], due to their high temperature and chemical stability. The structural characteristics of these materials can be modified when synthesized in nanosize together with good compositional homogeneity and stoichiometry [6–13]. They constitute a good class of combustion catalysts as they are found to be relatively stable in both oxidizing and reducing atmospheres [14]; however, sometimes they are less efficient. Attempts to enhance their efficiency include doping these perovskites with noble metals, such as Rh, Ag and Au [15–20]. Both A site and B site doping are possible bearing mixed valence states and enhanced mobility of oxygen in the lattice [21,22].

The method of synthesis adopted also influences the material properties significantly. Most popular methods of synthesis

include hydrothermal, spray pyrolysis, solid state reaction, microwave aided synthesis, sol–gel [23–39], etc.

In the present work, we report the synthesis of nanoparticles of silver doped lanthanum chromite for the first time. The samples were synthesized by microwave combustion method; partial doping at both A site and B site have been achieved with short reaction time of few minutes yielding perovskites of the types $\text{La}_{1-x}\text{Ag}_x\text{CrO}_3$ and $\text{LaCr}_{1-x}\text{Ag}_x\text{O}_3$. Further, the influence of dopant concentration, fuel/oxidizer ratio and precursor salts on material properties is investigated. Thus, the main purpose of this study is to explore the structural and ionic changes in the substituted perovskite with reference to pristine sample.

2. Experimental details

All the chemicals used were of A.R. grade. The salt precursors, i.e. lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and urea (NH_2CONH_2) as fuel were from Loba Chemie, India, while silver nitrate (AgNO_3) was from Qualigens, India. Lanthanum chromite was synthesized by initially mixing the precursor salts together in stoichiometric amounts, i.e. 1:1 equimolar ratio followed by the addition of urea as fuel (0.4 M), and to this was added $\sim 50\text{ ml}$ of double distilled water. The stoichiometric composition of the mixture

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was calculated based on the oxidizing valencies of metal nitrates and reducing valency of urea [40]. Silver doped samples were prepared by partial substitution of host atoms (La or Cr) by varying the concentration of added silver from 0.02 to 0.06 M, the molar concentrations of host atoms in the reaction were also varied proportionately. The resulting mixtures (for undoped and doped perovskites) were stirred for few minutes at room temperature and subjected to evaporation on a hot plate so as to obtain a gel. The gels were subjected to microwaves (0.1–0.9 kW power) using a domestic microwave oven (MG-555F Model) for auto combustion and the resulting products were cooled to room temperature. During synthesis, the fuel to oxidizer ratio was maintained as 1 while, the irradiation time was varied from 5 to 10 min so as to obtain pure phase products. The powders were characterized using various analytical techniques.

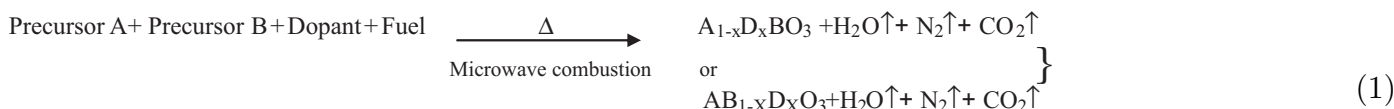
3. Characterization

Fourier transform infrared spectra (FTIR) of all the samples were recorded on a Shimadzu 8400 spectrophotometer over the range of 400–4000 cm^{-1} using KBr as a mulling agent. X-ray diffraction analysis of the powders was 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° to 80° at a scan rate of $0.1^\circ/\text{min}$. 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. Transmission electron micrographs (TEMs) 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. The TG–DTA curves of samples were recorded in an inert atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ using a Shimadzu instrument (Model DTG-60H). Lakeshore's Vibrating Sample Magnetometer (Model 7307) was used to perform magnetic measurements.

4. Results and discussion

The products were obtained through an exothermic reaction occurring between the reactant precursor's (metal nitrates) and urea as a fuel.

The combustion reaction can be represented as follows:



Precursor A ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Precursor B ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Dopant (AgNO_3) and Fuel (NH_2CONH_2)

During synthesis, the nitrates readily melt in their water of crystallization and aqueous solutions always absorb microwave radiations efficiently which are the source of energy. Additional heat is evolved upon oxidation of chromium which takes place during decomposition of nitrate salts. The evolved heat is the cause for continuous heating of sample after removal of water leading to decomposition of the precursors to give oxide phase.

The powder samples of LaCrO_3 , $\text{La}_{1-x}\text{Ag}_x\text{CrO}_3$, $\text{LaCr}_{1-x}\text{Ag}_x\text{O}_3$ (x refers to the fraction of La and Cr substituted by Ag) thus obtained were analysed using various analytical techniques. From the results, it was observed that the microwave power, oxidizer to fuel ratio and irradiation time determined the purity of the samples. At microwave power below 0.42 kW the product formation is not observed, at 0.42 kW partial product formation takes place while, 0.56 kW power yields pure phase product. At higher power levels the reaction is observed to be explosive in nature. The optimum irradiation time to obtain pure phase product is observed to be 10 min with an oxidizer to fuel ratio of 1.

4.1. FT-IR spectroscopy

Preliminary analysis of samples to ensure the formation of products was carried out by recording the FTIR spectrum of each of the products. Fig. 1(a) and (b) shows the FTIR spectra of as obtained samples and the one sintered at 800°C for 4 h, respectively. The absorption peaks at 600 and 400 cm^{-1} can be ascribed to Cr–O bond and O–Cr–O deformation vibrations indicating formation of product, while, narrow bands at $1085\text{--}1385 \text{ cm}^{-1}$ correspond to NO_3^- of unreacted precursor salts and N–H stretching is observed at 1485 cm^{-1} .

In Fig. 1(c) and (d) are given the FTIR spectra of silver doped (both A site and B site), lanthanum chromite samples which exhibit increment in band assignment of Cr–O stretching and O–Cr–O deformation vibrations implying substitution of Ag^+ ions at lanthanum and chromium sub lattice. The bands at 561 cm^{-1} and 443 cm^{-1} represent Ag–O bond formation.

The close frequency correlation of these bands in the spectra with those reported in the literature [41–43] confirms the presence of perovskite like oxide together with doping of silver (Ag^+) ions in A and B sub lattice.

4.2. X-ray diffraction analysis

Fig. 2 shows the X-ray diffractograms of the LaCrO_3 samples synthesized at 0.42 kW and 0.56 kW microwave power and the latter sample sintered at 200 and 800°C for a period of 4 h. Comparison of the X-ray diffractograms reveals the formation of pure phase product at microwave power of

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