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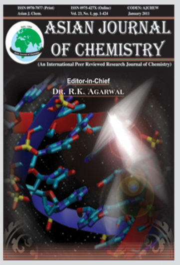

Synthesis of $LaCrO_3$ at Low Temperature by the Poly(vinyl alcohol) Gel Combustion Method

NGUYEN XUAN DUNG

Department of Chemistry, Vinh University, Vinh City, Vietnam

*Corresponding author: Tel: +84 383 855751; E-mail: dungdhv@gmail.com

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$LaCrO_3$ perovskite has been synthesized by the combustion of gel prepared from poly(vinyl alcohol) and metal nitrates at low temperature (700 ºC). $LaCrO_3$ was characterized by X-ray diffraction, thermogravimetric and differential thermal analysis, field emission scanning electron microscopy and brunaure-emmet-teller surface area. The optional preparative conditions were polyvinyl alcohol/metals 3:1 by mol, pH = 3-4 and 80 ºC for gel formation. The specific surface area of $LaCrO_3$ nanopowders was 14.1 m^2/g and average partial size was 60-70 nm.

Key Words: Poly(vinyl alcohol), Perovskite, Combustion method, $LaCrO_3$, Lanthanum chromite.

INTRODUCTION

Perovskite-type complex oxide, $LaCrO_3$, has been studied for utilization in solid-oxide fuel cell, high temperature-furnace electrode and as catalysts for the treatment of automobile exhaust[1-3].

The synthesis of perovskite at low temperature with small particle size and large specific square area is very interesting in heterogeneous catalysis. Conventionally, perovskites were synthesized *via* solid state reaction by heating constituent metal carbonates or sometime by precipitation (co precipitation)[4]. The method required heating of the solid reactants at high temperature (usually higher than 1000 ºC), so the specific surface area is low (< 5 m^2/g)[5-7].

In recent years, combustion synthesis has become an effective, low-cost method for production of various industrially useful materials. Today combustion synthesis has become a very popular approach for preparation of nanomaterials. The extensive research carried out in last five years emphasized the combustion synthesis capabilities for materials improvement, energy saving and environmental protection[8].

This paper deals with the synthesis of $LaCrO_3$ perovskite by the gel combustion method prepared from poly(vinyl alcohol) (PVA) and metal nitrates.

EXPERIMENTAL

The metal nitrate solution in the molar ratio La^{3+}/Cr^{3+} = 1:1 was mixed with the poly(vinyl alcohol). The green solution mixture was magnetically stirred at 80 ºC. As water evaporated, the solution turned into a very viscous gel. Gel was heated at 300 ºC for 1 h. After grinding, this material was further heated to form crystal phase.

The thermal analysis was performed on a DTA-50/TGA-50 apparatus (Shimadzu, Japan). X-Ray diffraction (XRD) experiments were carried out on a Siemens D-5005 diffractometer (Germany) with CuK_α radiation at a step size of 0.030º in the range 2θ from 10-70º. The FT-IR spectra were recorded in an Impact 410-Nicolet spectrometer (United States) between 3000 and 400 cm^{-1}.

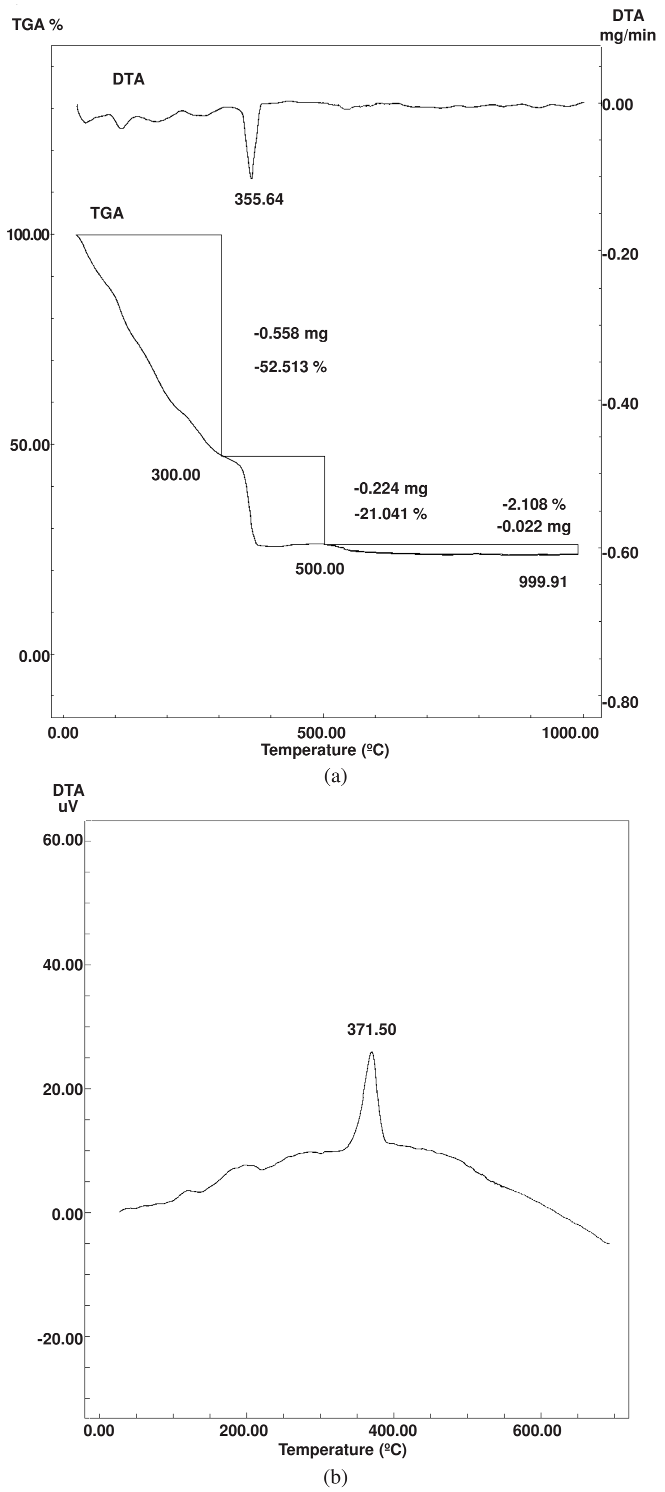
The BET specific surface areas were determined by nitrogen adsorption at 77 K using ASAP 2010 instrument (Micrometics, USA), operating in a single point mode.

The size and the shape of the particles were observed by field emission electron microscopy photographs using S 4800 instrument (Hitachi, Japan).

RESULTS AND DISCUSSION

Pyrolysis of gel: The pyrolysis of the gel-precursor was monitored by thermal analyses in Fig. 1. According to the TGA curve, the weight decrease terminated around 400 ºC. Before 300 ºC, the weight loss was associated with the removal of residual water and incomplete decomposition of poly(vinyl alcohol). In the range of temperature 300-500 ºC, the weight loss (accompanying exotherms in the DTA thermogram) showed the fire of poly(vinyl alcohol) being left in the gel with nitrates acted as an oxidizer. At a temperature higher than 500 ºC, the final weight loss corresponded to the formation of crystal phase.

Effect of heating temperature: Gels with PVA/metal mole ratio of 3:1 were prepared at 80 ºC, pH = 3 and heated at



(a)

(b)

Fig. 1. TGA-DTA curves of gel (a and b)

various temperatures (300, 400, 500, 600, 650, 700, 850 ºC). Fig. 2 presents XRD patterns of the obtained powders. Heating in the temperature range from 300-400 ºC results in an amorphous pattern. The XRD lines corresponding to $LaCrO_4$ began to appear at 500 ºC and the intensity increased up to 600 ºC. In the sample heated at 650 ºC, in addition to $LaCrO_4$ phase, the peaks of $LaCrO_3$ appeared more obvious. The samples above 650 ºC gave the characteristic XRD pattern of $LaCrO_3$. These results indicate that $LaCrO_4$ decomposed into $LaCrO_3$ at 700 ºC[9]:

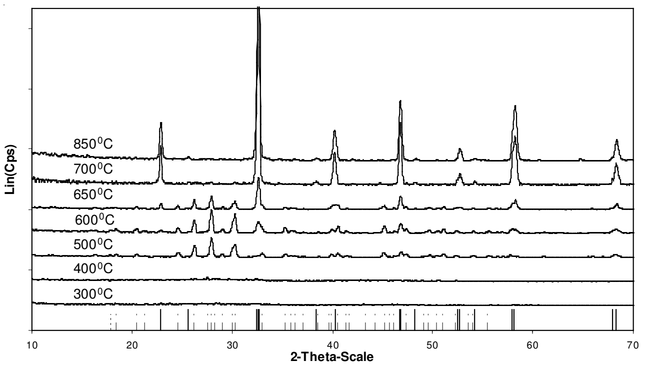


Fig. 2. XRD patterns of the powder samples prepared by heating the precursor at designated temperature for 1 h; lines (---) indicate the position of $LaCrO_4$ peaks [Ref. 10]; lines (—) indicate the position of $LaCrO_3$ peaks[11]

$$LaCrO_4 \longrightarrow LaCrO_3 + 1/2O_2$$

FTIR spectra taken from the powder samples prepared by heating the gel at 300, 400, 500, 600, 650, 700 and 850 ºC were shown in Fig. 3. Upon being heated at 300, 400 ºC, the peaks between 1510-1490 cm^{-1} suggested that poly(vinyl alcohol) moieties were destroyed and resultant carbonaceous residues were left in the precursor, one of which should be carbonate[12]. When the precursor was further heated at 500 to 600 ºC, the carbonate peaks disappeared and the peaks in the range 720-950 cm^{-1} were associated the with metal-oxygen vibration in $LaCrO_4$. Upon crystallization at 700 and 850 ºC, the absorption bands at 620-410 cm^{-1} were characterized by the metal-oxygen vibration in $LaCrO_3$[13]. The sample heated at 650 ºC showed metal-oxygen vibration in $LaCrO_4$ and $LaCrO_3$. From results above, we choose heating temparature 700 ºC to prepare samples.

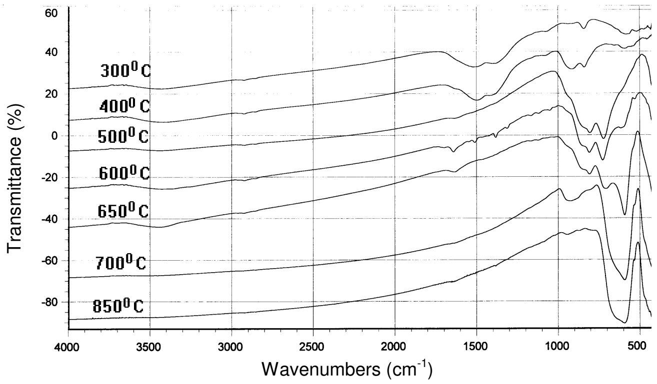


Fig. 3. FTIR spectra of samples heated at different temperatures (300, 400, 500, 600, 650, 700 and 850 ºC)

Effect of gel formating pH: Gels were prepared at 80 ºC, pH = 2-5 with PVA/metal mole ratio of 3:1 and were heated at 700 ºC for 1 h. Fig. 4 shows the XRD patterns of synthesized powders and the effect of pH on the crystal phase. In the powders prepared at pH 2 and pH 5, besides $LaCrO_3$ main phase, the diffraction peaks of $LaCrO_4$ were observed. At pH = 3-4, single phase crystalline $LaCrO_3$ was obtained. At high pH, we realise that PVA was separated from the gel solution and the combustion of gel was not completely. At low pH, PVA was not stable. Thus, we choose pH 3 to prepare samples in the next experiments.

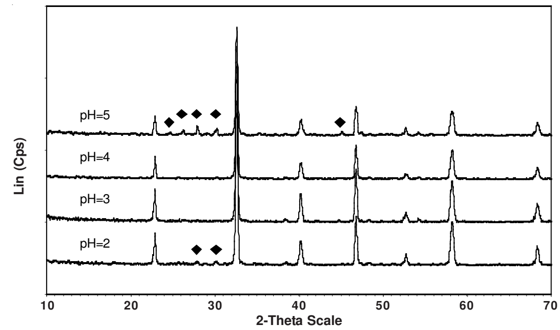


Fig. 4. XRD patterns of the powder samples prepared at pH = 2-5; ◆: phase $LaCrO_4$

Effect of PVA/metal mole ratios: Fig. 5 shows the stoichiometric effect of PVA/metals on the crystallization of precursor observed by XRD. In the case of precursor prepared with PVA/metal mole ratios 1:3 and 1:1, minor phase was observed (La_2CrO_6 for PVA/metal mole ratio 1:3, $LaCrO_4$ for PVA/metal mole ratio 1:1). When the amount of PVA added was small, the polar groups of the long chain of the polymer absorb only some of the cations present in the "precursor solution". This results in segregation and inhomogeneous distribution of the metal ions in the polymeric network structure of PVA, which finally culminated in multi-phase final product on complete evaporation of the PVA[14]. As the PVA/metal mole ratio increased in the gel, the precursor crystallized into a single phase $LaCrO_3$ without any minor phase. The use of PVA greatly suppressed the formation of minor phases by enhancing the homogeneity of the media[4]. In the following experiments, we used PVA/metal mole ratios 3:1 to prepare samples.

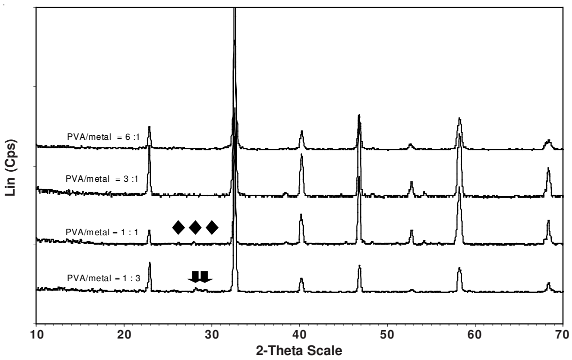


Fig. 5. XRD patterns of $LaCrO_3$ synthesized by heating gel precursors with various different PVA/metal mole ratios (1:3, 1:1, 3:1 and 6:1) at 700 ºC; ◆: phase $LaCrO_4$; ⬇: phase La_2CrO_6

Effect of gel formating temparature: Fig. 6 shows the XRD patterns of synthesized $LaCrO_3$ powders and the effect of the gel formating temparature on the crystal phase. In all powders, $LaCrO_3$ phase were observed. A small amount of $LaCrO_4$ phase was detected in the sample prepared from the gel formating at 95 ºC. At lower gel formating temparatures, the samples displayed $LaCrO_3$ single phase. However, at gel formating temparature 80 ºC, the peak intensity of the sample was largest.

The sample synthesized under optimal conditions (gel formating temparature 80 ºC, pH 3 and PVA/metal mole ratio of 3:1) were examined by FESEM and BET measurements. The results indicate that the estimated particle size was 60-70 nm and the specific surface areas was 14.1 m^2/g.

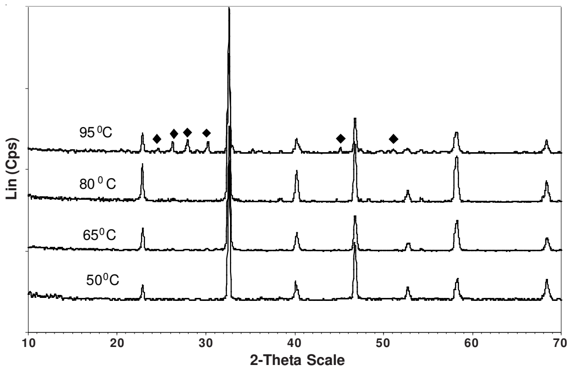


Fig. 6. XRD patterns of the powder synthesized from gels formating at different temparatures (50, 65, 80, 95 ºC); ◆: phase $LaCrO_4$

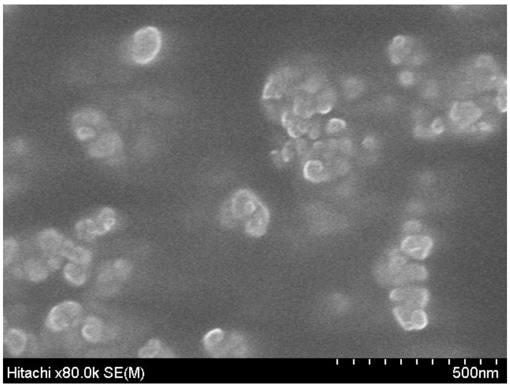


Fig. 7. FESEM of $LaCrO_3$ prepared under optimal conditions

Conclusion

Perovskite powder of $LaCrO_3$ was synthesized from the PVA gel combustion method at 700 ºC. Upon gel formated at 80 ºC, pH = 3-4 with PVA/metal mole ratio of 3:1, $LaCrO_3$ single phase was obtained. The sample prepared under optimal conditions has particle size 60-70 nm and the specific surface areas 14.1 m^2/g.

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