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Some investigation on nanocrystalline $LaCoO_3$ by combustion method

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ABSTRACT

This study reports on synthesis of nano sized $LaCoO_3$ mixed oxide was prepared by novel self combustion method using glycine as a fuel. The nanomaterial $LaCoO_3$ mixed oxide was characterized by TG-DTA, XRD, SEM, EDX and TEM. The average particle size of the nanomaterial $LaCoO_3$calculated from XRD was found in the range 50-60 nm .It was good agreement with TEM . The superhydrophilicity of the sintered oxides was investigated by wetting experiments, by the sessile drop technique, were carried out at room temperature in air to determine the surface and interfacial interactions.

Keywords: Nanomaterial, $LaCoO_3$, TG/DTA, XRD, SEM, EDX, TEM.

INTRODUCTION

Perovskite-type ABO_3 and related compounds have been reported to be of importance due to their wide uses in fuel cells [1], catalysts [2,3], membranes in syngas production [4], sensors [5,6] and environmental monitoring applications [7]. For the synthesis of LaFeO3 and relatedcompounds,methods involving solid-state reaction [8], hydrothermal synthesis [9], combustion synthesis [10,11], sol–gel [12–14], co-precipitation [15], reverse drop co precipitation with poly(vinyl alcohol) as a protecting agent [16], sonochemical method [17], thermal decomposition of La[Fe(CN)6] in conventional furnace [18–20] and citrate-gel method [21] have been reported in the literature. Several studies have reported that by finely controlling the micro/nanostructure or chemical composition of a surface, the adhesion between the superhydrophobic surface and water can be changed. Such superhydrophobic surfaces show potential in a variety of applications from antisticking, anticontamination and selfcleaning to anticorrosion and low friction coatings and gas sensing [22-23].

The present research, analyze the synthesis of an spinal $LaCoO_3$ by the combustion method with an average crystalline size of 50-60 nm.The superhydrophilicity of the sintered oxides was investigated by wetting experiments by the sessile drop technique was carried out at room temperature in air to determine the surface and interfacial interactions.

MATERIALS AND METHODS

In this study polycrystalline $LaCoO_3$ powder was prepared using combustion technique. The materials used as precursors were lanthanum nitrate hexahydrate La $(NO_3)_2.6H_2O$, cobalt nitrate hexahydrate Co $(NO_3)_2.6H_2O$ and glycine (all these were purchased from AR Grade of Qualigen fine Ltd.India). All of them were of high purity (99.9%, 98%, and 99.9% respectively). Glycine possesses a high heat of combustion. It is an organic fuel providing a platform for redox reactions during the course of combustion. Initially the lanthanum nitrate and cobalt nitrate are taken in the proportion 1:1:4 stoichiometric amount respectively and two moles of glycine were dissolved in a beaker slowly stirring by using glass rod clear solution was obtained. Then the formed solution was evaporated on hot plate in the temperature range of 70^{0}C to 80^{0}C resulting into a gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range of 170^{0}C to 180^{0}C. The nanocrystalline $LaCoO_3$ powder was formed within a few minutes. And it was sintered at about 500 ^{0}C about 4 hours then we got a black colour shining powder of nanocrystalline $LaCoO_3$.

The as –prepared samples were characterized by TG/DTA thermal analyzer (SDT Q600 V 20.9 Build 20), XRD Philips Analytic X-ray B.V. (PW-3710 Based Model diffraction analysis using Cu-K_α radiation), scanning electron microscope (SEM, JEOL JED 2300) coupled with an energy dispersive spectrometer (EDS JEOL 6360 LA), A JEOL JEM–200 CX transmission electron microscope operating at 200 kV analysis.

RESULTS AND DISCUSSION

6.1 TG-DTA

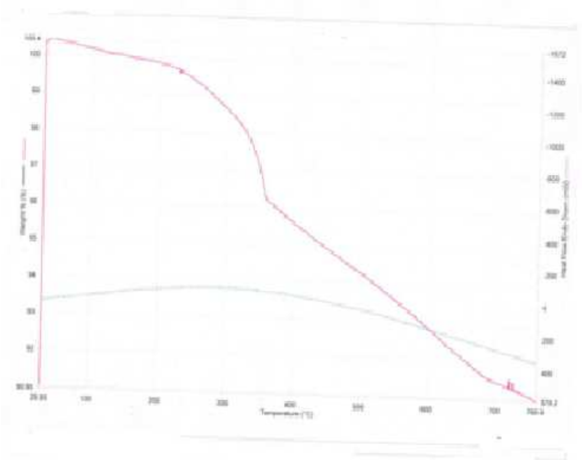

Fig.1 DTA-TG the prepared $LaCoO_3$ nominal composition

$$2C_2NH_3O_2 + (9/2)\,O_2 \;\rightarrow\; N_2\uparrow + 4CO_2\uparrow + 5H_2O \qquad (1)$$

$$La\,(NO_3)_3 + Co\,(NO_3)_3 + 4C_2H_5NO_2 \rightarrow LaCoO_3 + 8H_2O + 10H_2O + 5N_2\uparrow \qquad (2)$$

The TG cure recorded for thermal decomposition of $LaCoO_3$ is shown in (1). The cure indicates that the slight weight loss in $LaCoO_3$powder due to little loss of moisture, carbon dioxide and Nitrogen gas. The DTA curve of $LaCoO_3$ recorded in static air and is shown in Fig.1. The curve shows that $LaCoO_3$ did not decompose, but weight loss was due to dehydrogenation, decarboxylation and denitration and yield final product at 700^{0}C. This weight change was in the synthesized powder was almost remain stable from the beginning.

6.2 X-ray Diffraction study

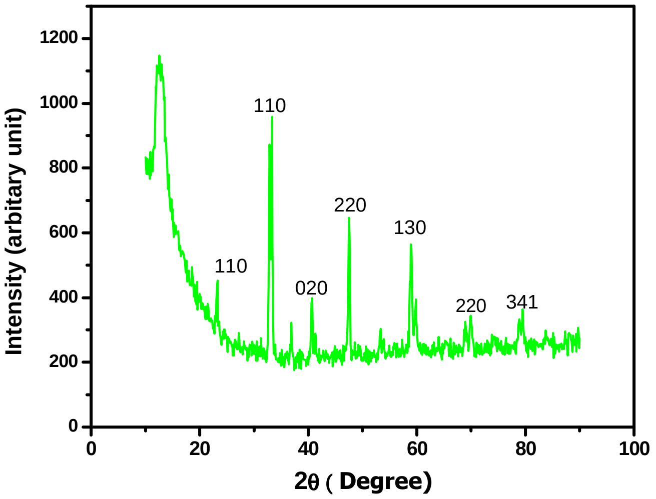

Fig.2. XRD pattern of calcinied mixed precursor $LaCoO_3$ at 700^{0}C, in air for 4 h.

The X-ray diffraction pattern of $LaCoO_3$ powder is shown in Figure 2. The observed 'd' values compared with standard 'd' values and were in good agreement with standard 'd' value matched with JCPDS data card number 84-0846. The structure possesses the Perovskite structure may be attributed to the different preparation method which may yield different structural defects. The crystalline size was determined from full width of half maximum (FWHM) of the most intense peak obtained by shown scanning of X-ray diffraction pattern. The grain size was calculated by using Scherer's formula [24,25]..

$$d = 0.9\lambda / \beta \cos\theta$$

Where,'d' is the crystalline size, λ is the X-ray wavelength of the Cu K_α source (λ=1.54056 A^0), β is the FWHM of the most predominant peak at 100 % intensity(110), θ is the Braggs angle at which peak is recorded. It was found at 60 nm.

6.3 Energy dispersive X-ray microanalysis studies (EDX)

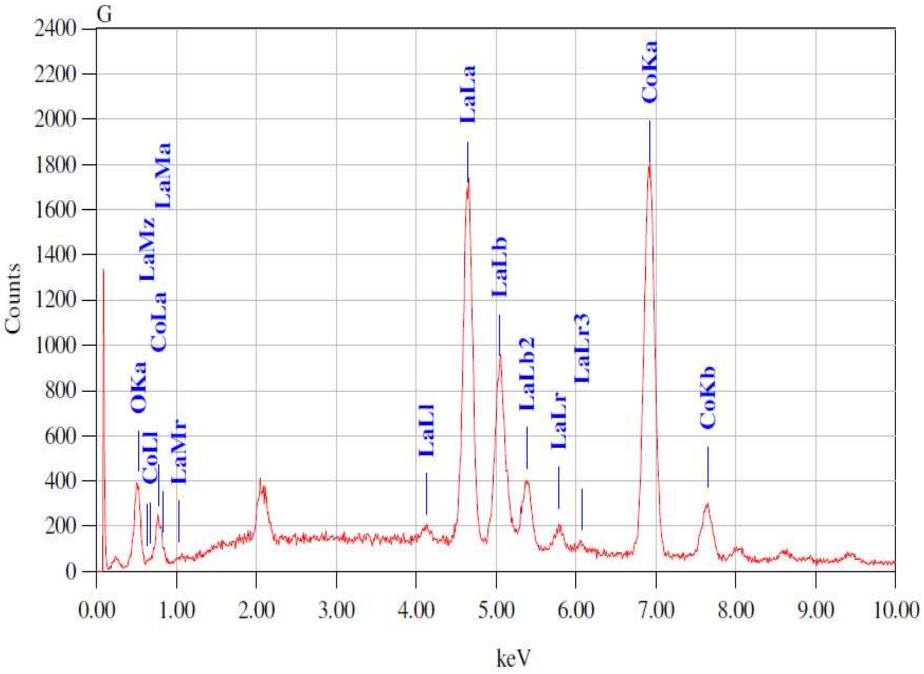

Fig.3. EDX pattern of mixed precursor $ZnCr_2O_4$ at 600^0C in air for 4 h.

Fig.3 shows the energy dispersive X-ray spectrum of $LaCoO_3$. This was carried out to understand the composition of Lanthanum, cobalt and oxygen in the material. There was no unidentified peak observed in EDX. This confirms the purity and the composition of the $LaCoO_3$ nanomaterial.

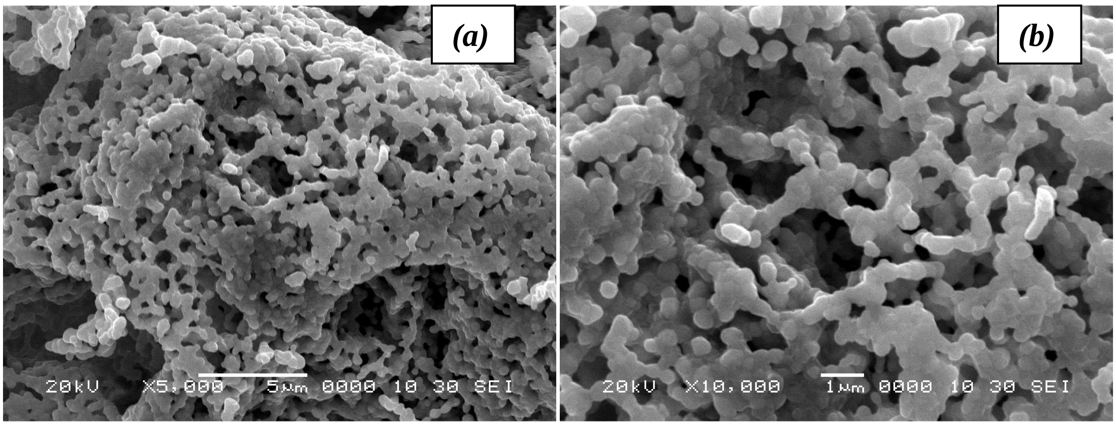

Fig.4. SEM images of mixed precursor $LaCoO_3$ at 700^0C in air for 4 h (a) low resolution and (b) high resolution.

6.4 Scanning electron micrograph study

The microstructure of the 700^{0}C sintered samples can be visualized from scanning electron microscope (SEM) tool. Fig. 4 (a,b)depicts SEM images of $LaCoO_3$ powder it shown the particle morphology of high resolution the particle are most irregular in shape with a nanosized range of 50-200 nm some particles are found as agglomerations containing very fine particles. It can be observed that $LaCoO_3$ have uniformed size. It seems that surfaces are smooth, spongy and pores are seen in the micrograph.

6.5 Transmission electron microscopy (TEM)

The TEM image of the mixed precursor calcined at 700^{0}C for 2h are shown in Fig.(a,b) 5. It indicates the presence of $LaCoO_3$ nanoparticles with size 50-60 nm which form beed type of oriental aggregation throughout the region. No evidence was found for more than one pattern, suggesting the single phage nature of the material.

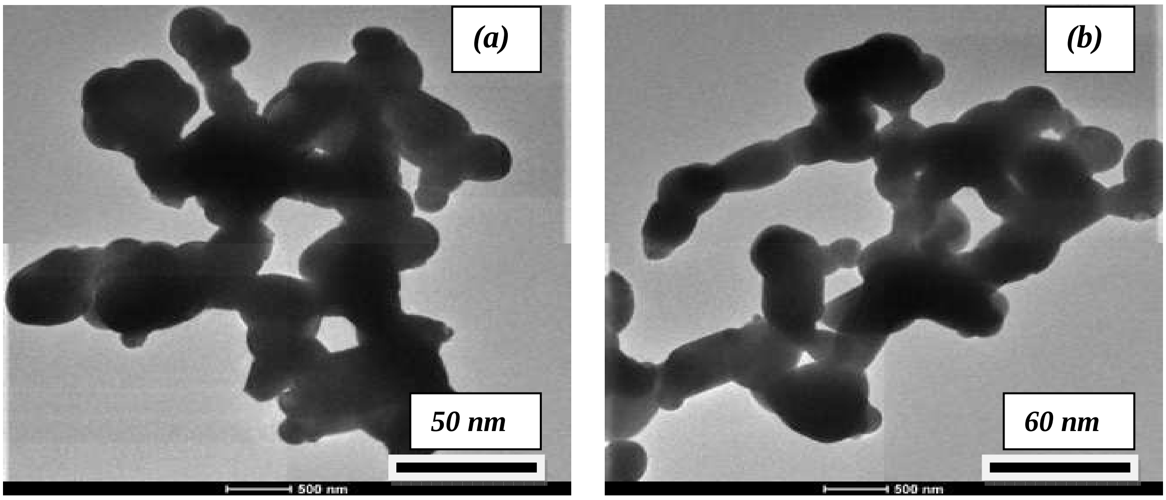

Fig.5 TEM (a,b) images of mixed precursor $LaCoO_3$

7. Superhydrophilic Test

Wet ability of pallet shows behaviour of water droplet on upper surface of material depends on surface energy and surface roughness of material. Thomas Young had described the force acting on a liquid droplet spreading on surface so-called contact angle (θ) is related to interfacial energies acting between the solid-liquid (γ_{SL}), solid-vapor (γ_{SV}) and liquid-vapor (γ_{LV}) given by following relation.

$$\cos\theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (2)$$

The expression given by Equation 2 is strictly valid only for surfaces that are atomically smooth, chemically homogeneous and those that don't change their characteristics due to interactions of the probing liquid with the substratum or any other outside force. Wenzel regime liquid wets the surface but the measured contact angle θ* differs from the "true" contact angle θ by Wenzel's equation for rough surface r > 1.

$$\cos\theta^{*} = r\cos\theta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where r is the roughness factor of the 9/surface. The wet ability nature of our synthesized material is super hydrophilic in the Wenzel because of highly rough surface nature was clearly seen from SEM images with consideration given to the surface roughness. Fig. 6 (a-b) shows the image of contact angle on rough surface of lanthanum cobalt oxide material. It was seen that contact angle of material is θ =0 hence material in superhydrophilic θ≤5 may be due to high energy surface and their porous nature.

In to characterization

Wetting experiment of synthesized pure lanthanum cobalt oxide evaluated by contact angle measurement were performed by the sessile drop method using advanced goniometer apparatus (Model110, Ram hart Instrument Co., USA) and distilled water droplets of 0.01ml were delivered to surface of lanthanum cobalt oxide pellet material at different points.

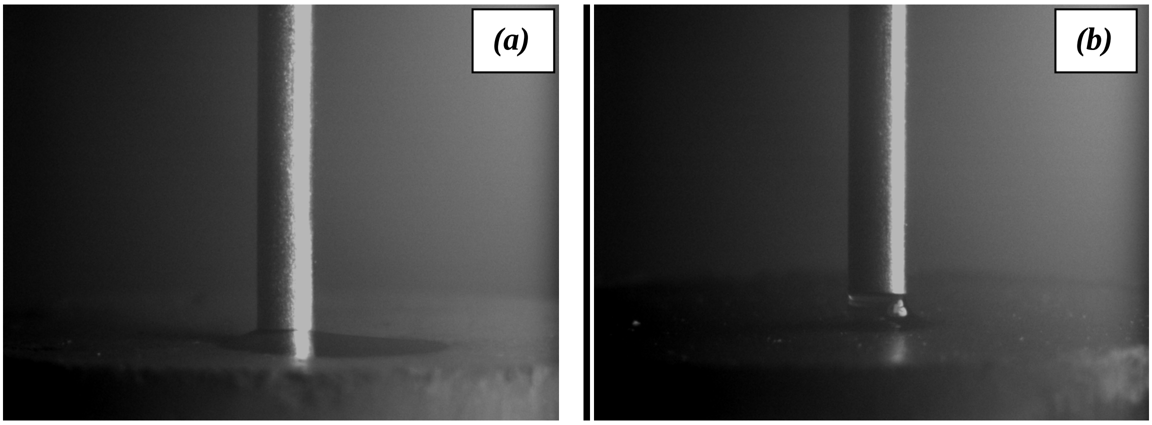

Fig.6 (a-b) Photograph of measured contact angle on rough surface of lanthanum cobalt oxide (pellet) material.

CONCLUSION

Nanocrystalline $LaCoO_3$ has been successfully synthesized by self combustion route. TG-DTA analysis indicates the phase formation was carried out at 700^0C. The route may be used for the synthesis of other metal oxide. XRD technique was shown the average crystal size of the $LaCoO_3$ nanoparticles ranges from about 60 nm at 700^0C respectively. Elemental analysis confirmed by using EDX. SEM micrographs show the material is porous in nature. TEM image shows grain size of the material was 50-60 nm. Wetability of this material obtained from contact angle goniometer. The contact angle θ was zero, which indicates that oxide material was superhydrophilic in nature.

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