

SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE LaCrO_3 BY COMBUSTION ROUTE

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ABSTRACT

Lanthanum chromate LaCrO_3 , an important catalyst and interconnect material used in solid oxide fuel cell was prepared from lanthanum nitrate hexahydrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (LN), chromium nitrate nonahydrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (CN) and glycine. The mixture was heated in Pyrex disc, resulting the formation of pure LaCrO_3 at 180°C within five minutes. Other methods give LaCrO_3 at 900°C . BET surface area of LaCrO_3 prepared by combustion method was found to be $3.0 \text{ m}^2/\text{g}$. Thermogravimetry, Differential thermal analysis, X-ray diffraction SEM techniques and atomic fluorescence microscopy (AFM), were used to characterize the LaCrO_3 . Average particle size determine by Debye Scherrer's equation was found to be $\sim 16\text{nm}$.

Keywords: Catalyst, LaCrO_3 , combustion method, TG-DTA, XRD, SEM, and AFM.

INTRODUCTION

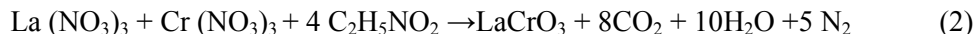
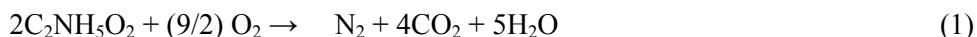
LaCrO_3 is chemically stable in both reducing as well as oxidizing atmosphere. The doped LaCrO_3 shows high electrical conductivity therefore used as separator material in solid oxide fuel cell (SOFC)¹⁻³. It is also used as hot electrode for magneto hydrodynamic [MHD] power generation⁴. It was also investigated for its catalytic activity in catalytic combustion of methane⁵. Doped LaCrO_3 shows oxygen ion conductivity and has been studied for its applications in oxygen sensors and oxygen permeable membrane.⁶⁻⁸ Preparations of LaCrO_3 by various methods are reported in the literature, these methods include Pechini method⁹, conventional method¹⁰, sol-gel method¹¹, citrate method¹², oxalate route¹³ and microwave heating method¹⁴. All these methods yield LaCrO_3 after heating mixture of precursors at high temperature (500 - 1000°C) for long time (1-12 hr.). Combustion method was however used recently more effectively to bring down the temperature as well as time required for the synthesis of mixed oxides¹⁵⁻¹⁸. In this paper, we show that it is possible to synthesize LaCrO_3 within 5 minutes at low temperature employing combustion method.

EXPERIMENTAL

Polycrystalline LaCrO_3 was synthesized by the combustion synthesis method using glycine as fuel (organic fuel). All chemical reagents were analytical grade and used without further purification. Stoichiometric quantity of solid mixture of one mole reagents i.e. Lanthanum nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and two mole of glycine were mixed together in a flat Pyrex disc. The solid were stirred for five minutes (clear solution was obtained). Solution formed was evaporated on hot plate in temperature range 80 - 90°C gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range of 160 - 180°C . The nanocrystalline LaCrO_3 powder was formed within five minutes. Surface area of LaCrO_3 prepared was measured by BET nitrogen gas adsorption method.

RESULTS AND DISCUSSION

When reactants were heated at 180°C the reaction proceeds by the mechanism indicated by equation number 1 and 2 give the final product LaCrO_3 .



The TG curve recorded for thermal decomposition of LaCrO_3 is shown in Fig.1. The curve indicates that the slight weight loss in LaCrO_3 powder due to little loss of moisture, carbon dioxide and nitrogen gas. The DTA curve of LaCrO_3 recorded in static air and is shown in Fig.2. The curve shows that LaCrO_3 did not decompose, but weight loss was due to dehydrogenation decarboxylation and denitration and yield final product at 775°C . This weight loss and weight gained was very negligible. This weight change was in the range of 0.02 % only. These indicate that the synthesized powder was almost stable from the begging.

X-ray diffraction XRD measurements were performed on Philips Analytic X-ray B.V. (PW-3710 Based Model) Advanced X-ray diffraction using $\text{Cu K}\alpha$ 1.54056, radiation. The XRD pattern shown in the fig.(2).The XRD pattern shows that the product is pure perovskite oxide LaCrO_3 with an orthorhombic structure. The diffraction data are good agreement with JCPD card of LaFeO_3 (JCPDS No.24-1016) The average crystalline size of LaCrO_3 spinel powder is calculated from X-ray line broadening, using Scherrer's formula $t = 0.9\lambda / \beta \cos\theta$ ¹⁹⁻²⁰ where t is the thickness of the crystals (in angstroms), λ the X-ray wavelength and θ the Bragg angle β is the integral breadth that depends on the width of the most predominant peak at 100% intensity = $1.54056 \text{ \AA}$, the wavelength of the $\text{Cu K}\alpha$ source and θ is the Bragg's angle at which the peak is recorded. The orthorhombic lattice parameter obtained for the as synthesized powder ($a = 5.479 \text{ \AA}$, $b = 5.513$ & $c = 7.756 \text{ \AA}$) are comparable to that of bulk sample (5.592...). The slight smaller value of lattice parameter of the nanomaterials is a common feature observed for nanosized materials due to the lattice contraction in fine particles as well as due to a difference in the distribution of different metals in A and B sites of the spinel structure. The average particle size of nanocrystalline LaCrO_3 was ~16 nm. The as synthesized nanocrystalline single phase powder obtained by the modified GNP is further annealed in air at 850°C temperature for 4 hrs showed in fig. 3. The average particle size was unchanged. LaCrO_3 nanocrystals are more attractive in the field of catalytic application. The surface morphology was studied by using scanning electron microscopy (SEM) Model No. JEOL, JSM.6360. The SEM images of LaCrO_3 are shown in fig. (4).The SEM images reveal the product is a low density, loose and porous material that is favorable to a catalyst application. The BET surface areas were measured on a Benchman coulter SA 3100 plus instrument using nitrogen adsorption at 200°C . the surface area of the synthesized powder was $3.5 \text{ m}^2/\text{g}$.

Scanning Electron Microscope (SEM) image of the LaCrO_3 powder prepared by combustion method at 180°C is presented in Fig.4. (a) SEM images at 510°C and 850°C are shown in fig.4(b) and fig. 4(c) respectively. It shows that average particle size of LaCrO_3 formed is ~16nm. The particle size was also calculated from atomic fluorescence microscopy (AFM) recorded at 450°C and 1000°C temperatures. AFM images are shown in fig.5. Particle size increases as the temperature increases.

CONCLUSION

The following conclusions can be made from the present experiment.

1. LaCrO_3 can be simply synthesized chemically by glycine combustion method.
2. The obtained LaCrO_3 crystals with fine particle size of nanometer give a relatively high value of surface area of about $3.5 \text{ m}^2/\text{g}$.
3. This method can be also applicable for other complex oxides such as LaFeO_3 and we foresee that the LaCrO_3 nanocrystals are more attractive in the field of catalytic application and process can be applied to prepared more other oxide nanocrystals.

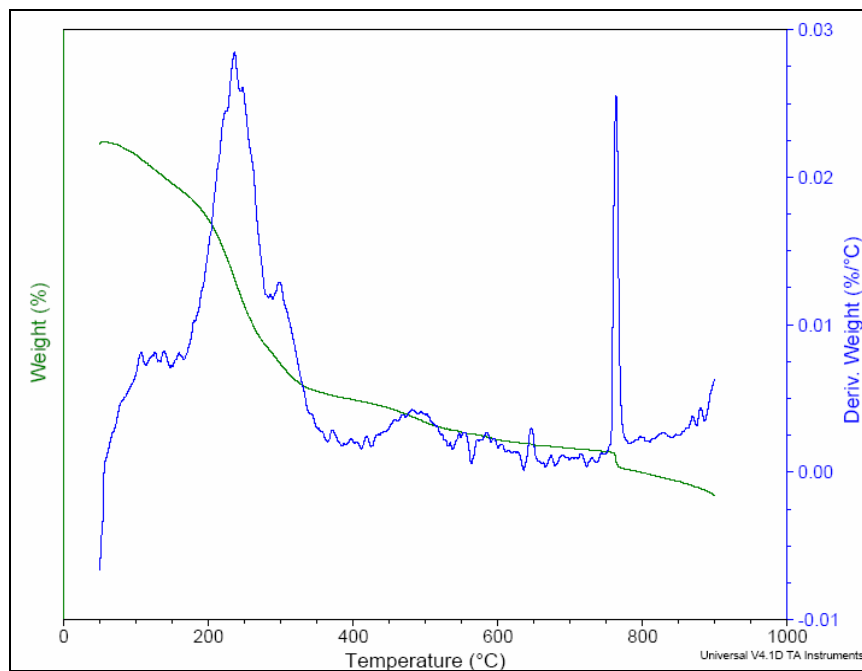


Fig.-1: TG - TDA curve of LaCrO₃ as synthesized powder.

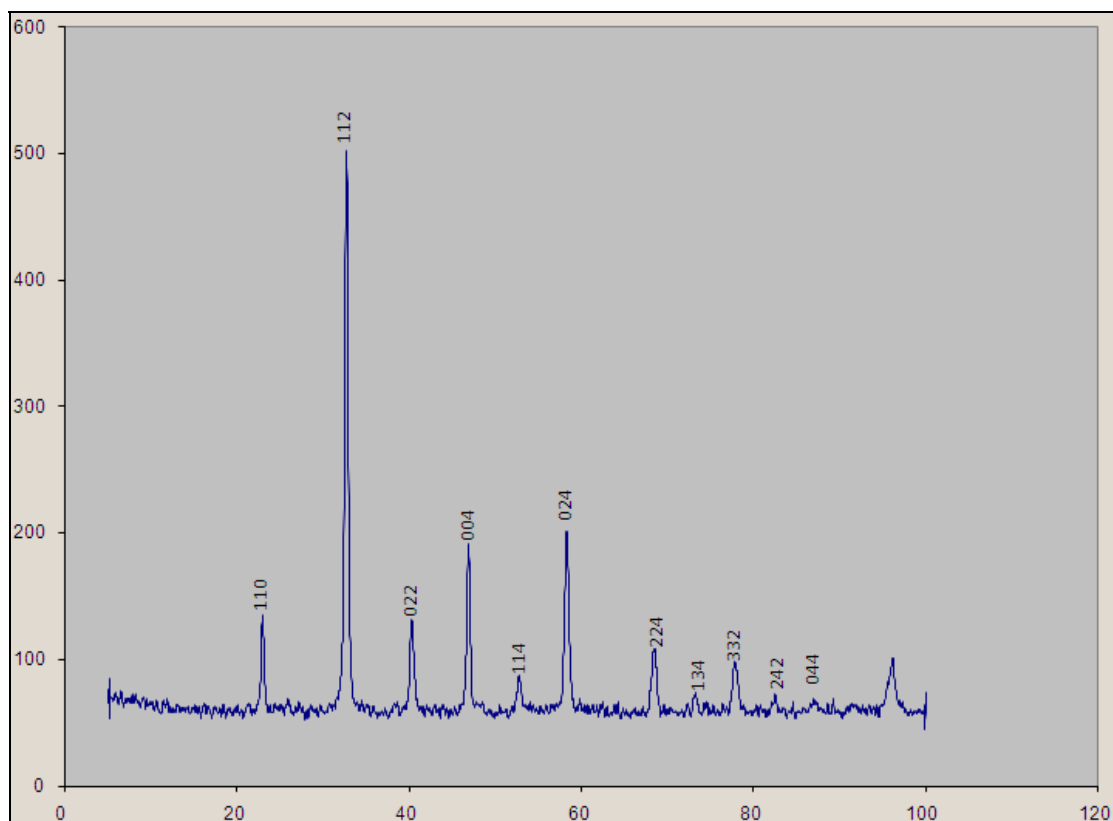


Fig. -2: XRD pattern of LaCrO₃ as synthesized powder.

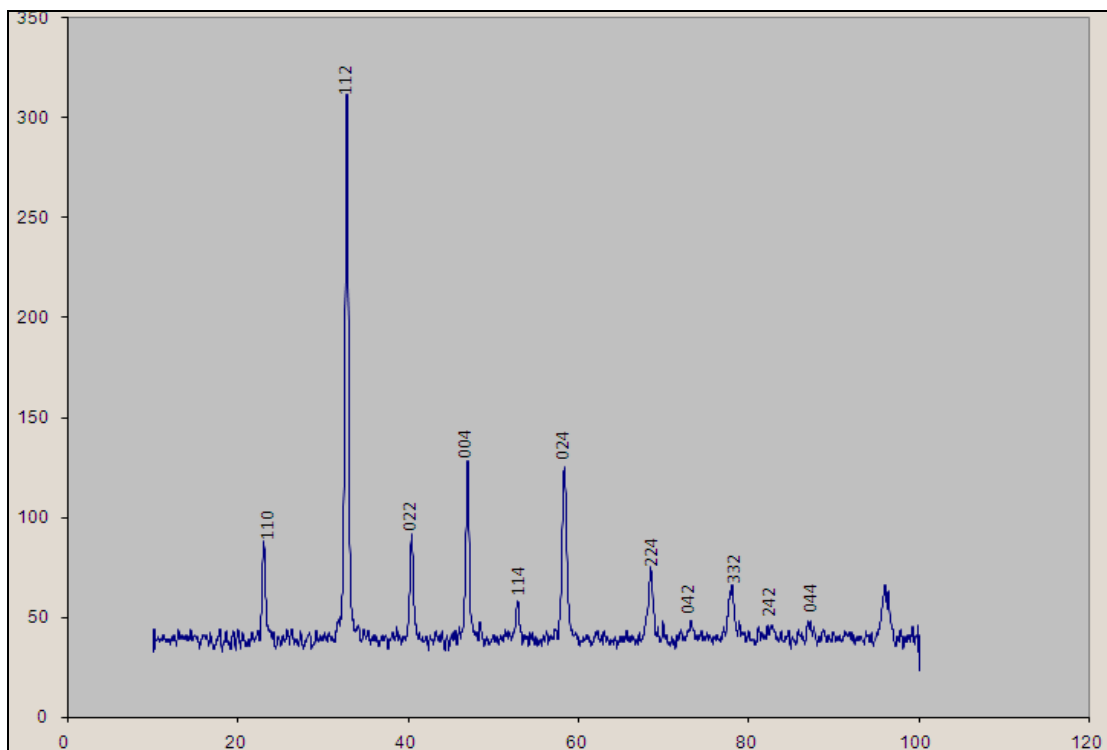


Fig.-3: XRD Pattern of LaCrO_3 sintered at 850°C for 4 hrs.

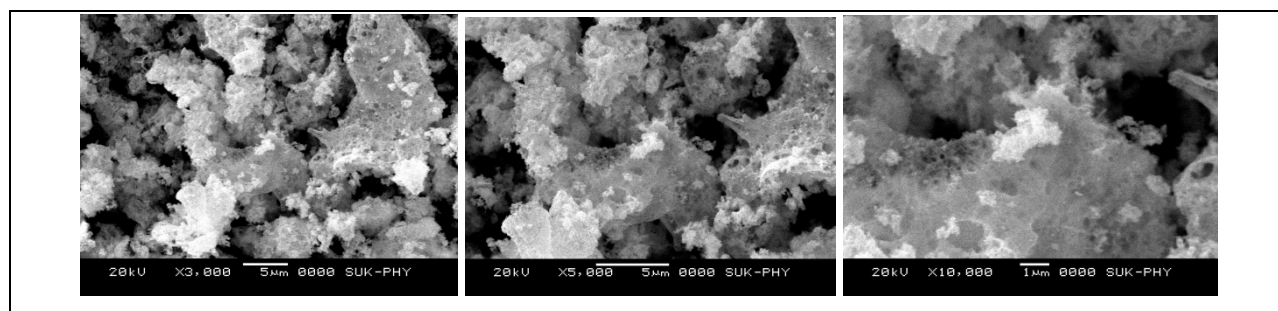


Fig.-4 (a): SEM images of LaCrO_3 as synthesized powder

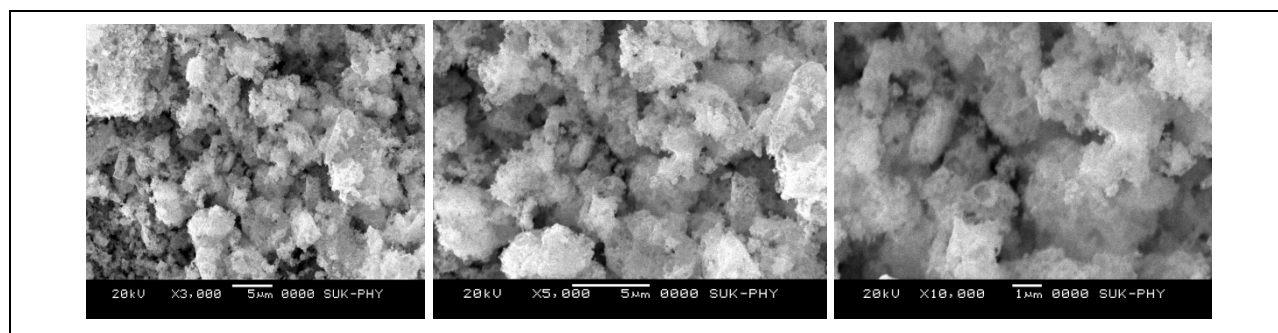


Fig.-4 (b): SEM images of LaCrO_3 powder at 510°C .

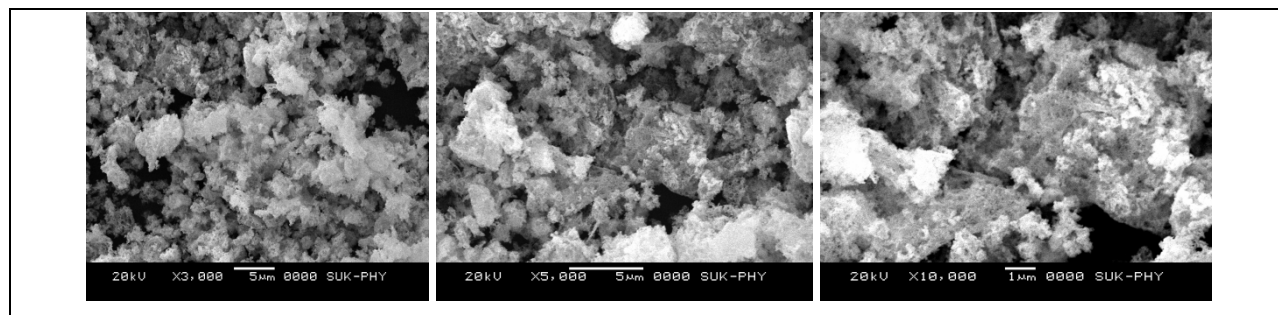


Fig.-4 (c) :SEM images of LaCrO_3 powder at 850°C

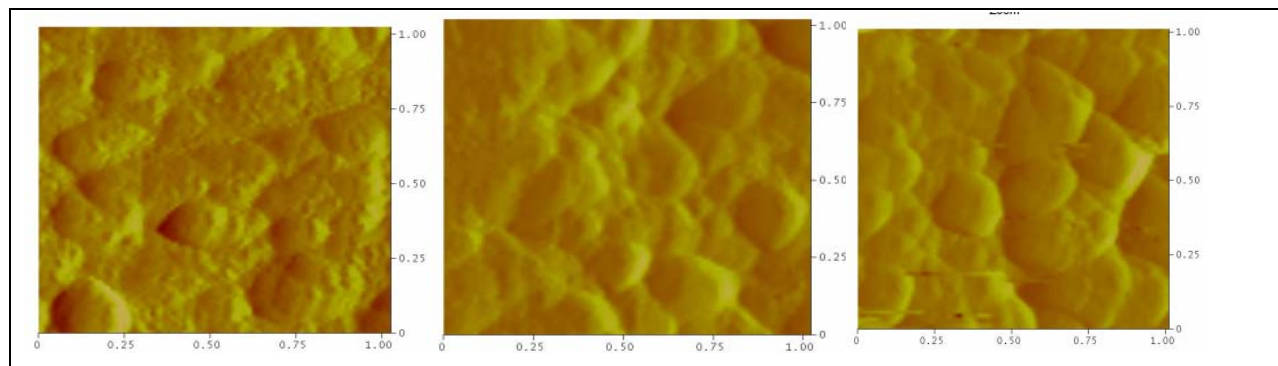


Fig.- 5: AFM images of LaCrO_3 pellet samples heated at 450°C and 1000°C

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