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SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE $LaCrO_3$ BY COMBUSTION ROUTE

S. M. Khetre[1], H. V. Jadhav[2]and S. R. Bamane[3*]
[1]Mahatma Phule A.S.C.College Panvel, Navi-mumbai 410206, India
[2]Kisanveer Mahavidhyala, Wai, Satara
[3]Dr. Patangrao Kadam Mahavidhyala Sangali India.
[*]E-mail:sambhajibamane@yahoo.comm

ABSTRACT
Lanthanum chromate $LaCrO_3$, an important catalyst and interconnect material used in solid oxide fuel cell was prepared from lanthanum nitrate hexahydrate La $(NO_3)_3.6H_2O$ (LN), chromium nitrate nonahydrate Cr $(NO_3)_3.9H_2O$ (CN) and glycine. The mixture was heated in Pyrex disc, resulting the formation of pure $LaCrO_3$ at 180^{0}C within five minutes. Other methods give $LaCrO_3$ at 900^{0}C. BET surface area of LaCrO3 prepared by combustion method was found to be 3.0 m^2/g. Thermogravimetry, Differential thermal analysis, X-ray diffraction SEM techniques and atomic fluorence microscopy (AFM), were used to characterize the $LaCrO_3$. Average particle size determine by Debay Scherrer's equation was found to be ~16nm.
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 generation[4]. It was also investigated for its catalytic activity in catalytic combustion of methane [5] 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 method[9], conventional method[10], sol-gel method[11], citrate method[12], oxalate route[13]and microwave heating method[14]. All these methods yield $LaCrO_3$ after heating mixture of precursors at high temperature (500-1000^{0}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 oxides[15-18]. 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 La $(NO_3)_3.6H_2O$, Cr $(NO_3)_3.9H_2O$ 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^{0}C gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range of 160-180^{0}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^{o}C the reaction proceeds by the mechanism indicated by equation number 1 and 2 give the final product LaCrO3.

$$2C_2NH_5O_2 + (9/2)\, O_2 \rightarrow \quad N_2 + 4CO_2 + 5H_2O \qquad (1)$$

$$La\,(NO_3)_3 + Cr\,(NO_3)_3 + 4\, C_2H_5NO_2 \rightarrow LaCrO_3 + 8CO_2 + 10H_2O + 5\, N_2 \qquad (2)$$

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 775^0C. 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 Cu Kα 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 $t = 0.9\lambda/\beta cos\theta\beta$ [19-20] where t is the thickness of the crystals (in angstroms), λ the X-ray wavelength and θβ the Bragg angle β is the integral breath that depends on the width of the most predominant peak at 100% intensity =1.54056 A^o, the wavelength of the Cu Kα 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 = 5.479A, b = 5.513 & c = 7.756 A^0) 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 850^0C 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 200^0 C. the surface area of the synthesized powder was 3.5 m^2/g.

Scanning Electron Microscope (SEM) image of the $LaCrO_3$ powder prepared by combustion method at 180^0C is presented in Fig.4. (a) SEM images at 510^0C and 850^0C 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 fluroscence microscopy (AFM) recorded at 450^0Cand 1000^0C 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 m^2/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.

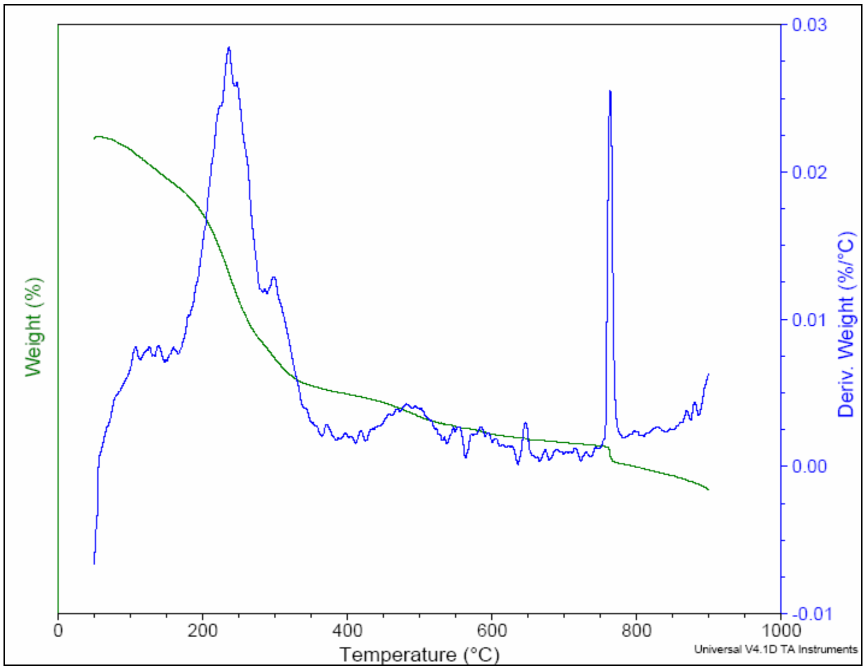

Fig.-1: TG - TDA curve of $LaCrO_3$ as synthesized powder.

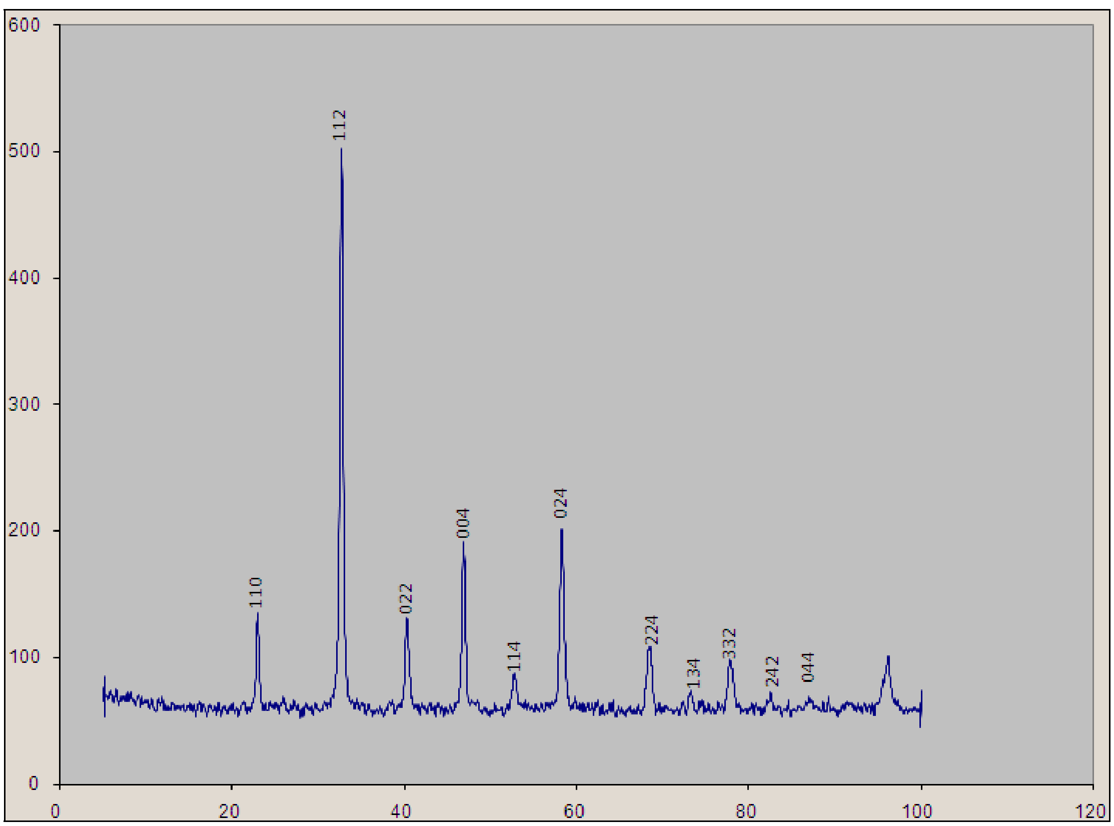

Fig. -2: XRD pattern of LaCrO3 as synthesized powder.

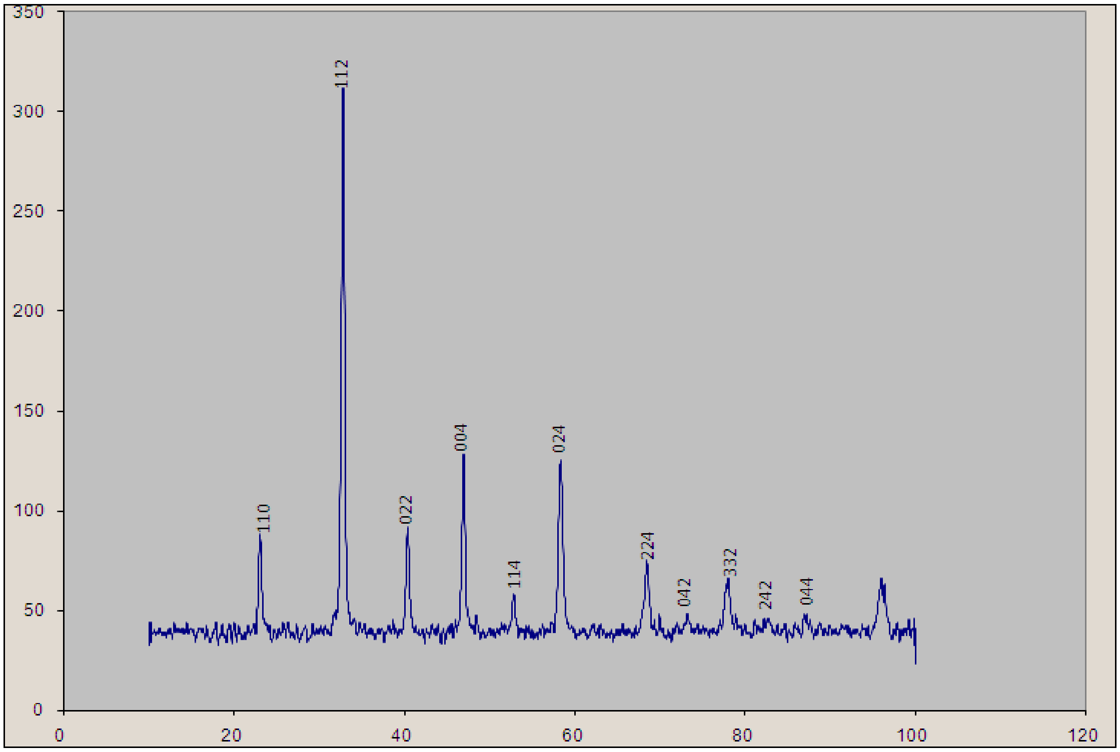

Fig.-3: XRD Pattern of LaCrO3 sintered at 850^0C for 4 hrs.

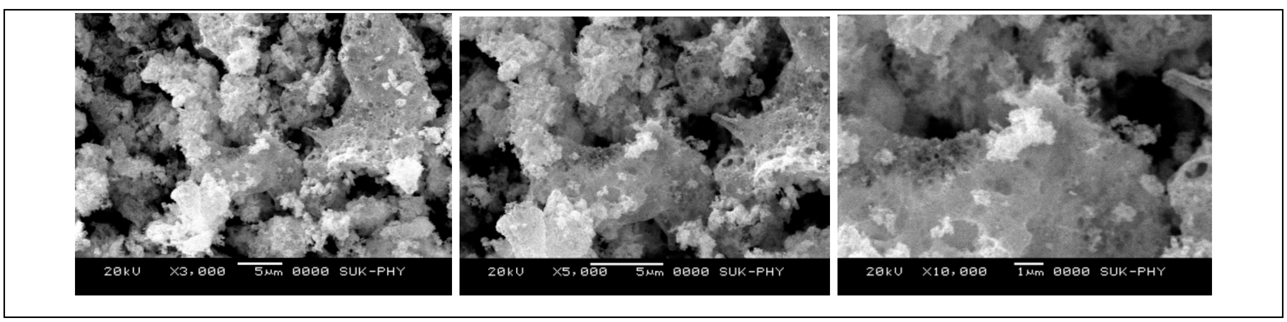

Fig.-4 (a): SEM images of $LaCrO_3$ as synthesized powder

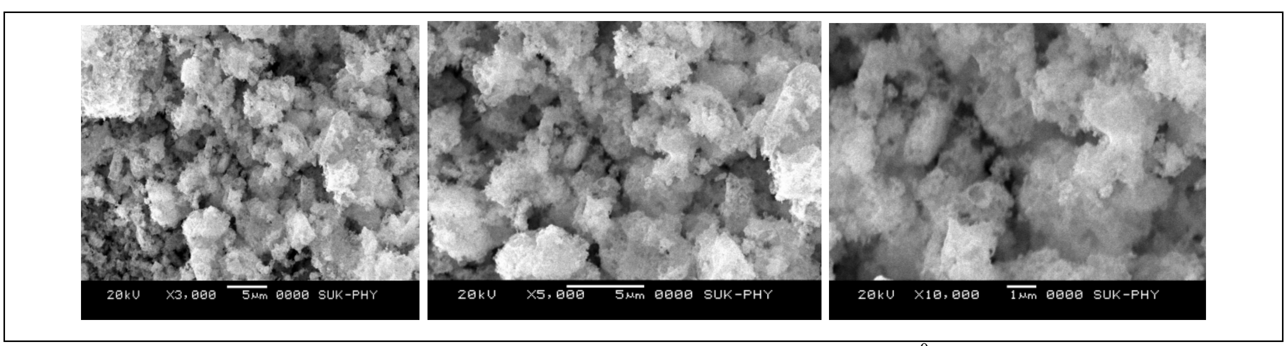

Fig.-4 (b): SEM images of $LaCrO_3$ powder at 510^0C.

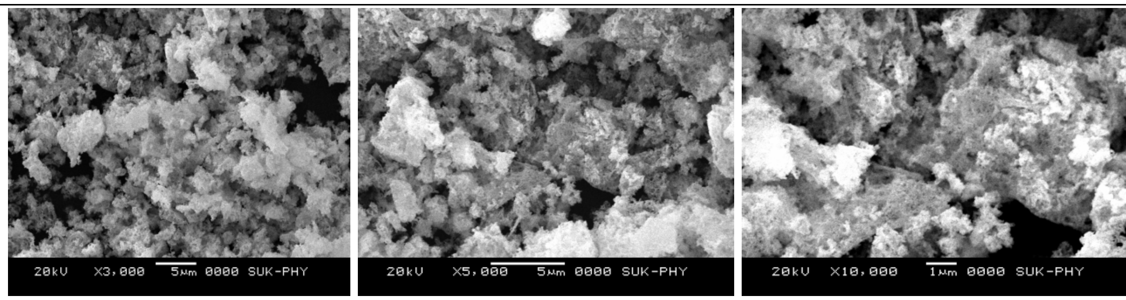

Fig.-4 (c) :SEM images of $LaCrO_3$ powder at 850^0C

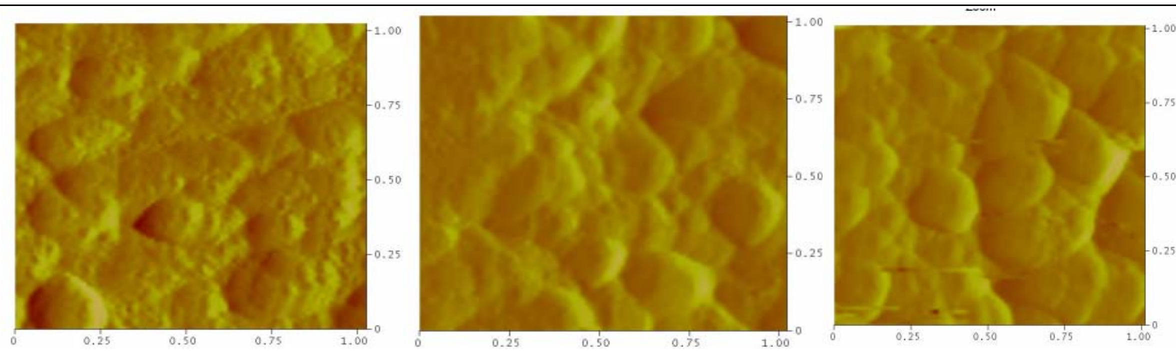

Fig.- 5: AFM images of LaCrO3 pellet samples heated at 450^0C and 1000^0C

REFERENCES

1. B. C. Steele and A. Heinzel, Nature, **414**, 345 (2001).
2. A. Hammou and J. Guindet, The CRC Handbook of Solid State Electrochemistry' (Eds. P. J. Gellings and H. J. M. Bouwmeester), CRC Press Lnc., 407 (1997).
3. P.S. Devi, A.D. Sharma and H.S. Maiti, *Transactions of Indian Ceramic Society*, **63** (2004).
4. D.B. Meadowcraft and J.M. Wimmer, *Ceramic Bulletin*, **58**, 610 (1979).
5. S.J. Chao, K.S. Song, I.S. Ryu, Y.S. Seo, M.W. Rayoo and S.K. Kang, *Catalysis Letters*, **58**, 63 (1999).
6. N.Q. Minh, *J. Amer. Ceram. Soc.*, **76** , 563 (1993).
7. A.S. Mukasayan, C. Costello, K.P. Sherlock, D. Lafarga and V. Nerma, *Separation and Purification Technology*, **25**, 117 (2001).
8. B.C.H. Steele, *Mater. Sci. Eng.*, **B13**, 79 (1992).
9. M. Mori and N.M. Sammes, *Solid State Ionics*, **146**, 301 (2002).
10. A. Wold and R. Ward, *J. Amer, Chem. Soc*., 76, 1029 (1954).
11. S. Bilger, G. Blass and R. Forthmann, *J. Eur. Ceram. Soc*., **17**, 1027 (1997).
12. P.S. Devi and M. Suba Rao, *Therchim. Acta*, **153**, 181 (1989).
13. A. Rao and K. Nag, *J. Inorg. Nucl. Chem*., 40, 1501 (1978).
14. Y.S. Malghe and S.R. Dharwadkar, *Journal of Thermal analysis and Calorimetry*, **91**, 915 (2008).
15. A.H. Naik, N.V. Thakkar, S.R. Dharwadkar, K.D. Singh Mudher and V. Venugopal, *Journal of Thermal analysis and Calorimetry*, **78**, 707 (2004).
16. Y.S. Malghe, A.V. Gugar and S.R. Dharwadkar, *Bull.Mater. Sci.,* **27**, 217 (2004).
17. O. Palchik, J. Zhu and A. Gedanken, *J. Mater. Chem.*, **10**, 1251 (2000).
18. Y.S. Malghe, A.V. Gugar and S.R. Dharwadkar, *Journal of Thermal analysis and Calorimetry*, **78**, 739 (2004).
19. P. Crambelli et al., *Turco,Appl.Catal.B*, **24**, 243 (2000).
20. B.D. Cullity, *Elements of X-ray diffraction*,Addison-Wesley, Londan, p.99 (1956).

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