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# $LaCrO_3$ POWDER FROM LANTHANUM TRISOXALATOCHROMATE(III) (LTCR) PRECURSOR

## Microwave aided synthesis and thermal characterization

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Lanthanum chromite $LaCrO_3$, an important catalyst and interconnect material used in solid oxide fuel cell was prepared from lanthanumtrisoxalatochromate(III) hydrate $[LaCr(C_2O_4)_3]\cdot 9H_2O$ (LTCR) employing microwave heating technique. The compound LTCR heated in microwave heating system gave pure $LaCrO_3$ at 500°C within one hour. However LTCR heated in silicon carbide furnace yielded $LaCrO_3$ at 900°C. BET surface area of $LaCrO_3$ prepared by microwave and conventional heating techniques were found to be 2.8 and 1.2 $m^2\ g^{-1}$, respectively. Thermogravimetry, differential thermal analysis and X-ray diffraction techniques were used to optimize the conditions for the microwave processing of the precursor.

***Keywords:*** *catalyst, $LaCrO_3$, microwave heating, solid oxide fuel cells*

## Introduction

$LaCrO_3$ is chemically quite stable in both oxidizing as well as reducing atmosphere. The doped $LaCrO_3$ shows high electronic conductivity and hence used as separator/interconnect material in solid oxide fuel cells (SOFC) [1–3]. $LaCrO_3$ is also used as hot electrode for MHD (magnetohydrodynamic) power generation [4]. It was also investigated for its catalytic activity in combustion of $CH_4$ [5]. Doped $LaCrO_3$ shows oxygen ion conductivity and has been studied for its applications in oxygen sensors and oxygen permeable membranes [6–8].

Solid-state synthesis of large number of oxides of transition metals and the compounds formed by their interaction with the oxides of other elements has been attempted via thermal decomposition of the carboxylates [9–13] of these elements. Synthesis of $LaCrO_3$ by various methods is reported in the literature. These include conventional method [14], combustion method [15], Pechini method [16], sol–gel method [17], citrate route [18], oxalate route [11], etc. All these methods yield $LaCrO_3$ after heating mixture of reactants/precursor at high temperature (600–1000°C) for long time (4–12 h). Microwave technique was however used recently, more effectively to bring down the temperature as well as time required for the synthesis of mixed oxides [12–13, 19, 20]. In this paper, we show that it is possible to employ the same method for the synthesis of $LaCrO_3$. In the present work $LaCrO_3$ was synthesized from LTCR precursor employing microwave heating technique.

## Experimental

### *Materials*

Lanthanum nitrate $La(NO_3)_3\cdot 6H_2O$ (LN) used for $LaCrO_3$ synthesis, was of AR grade and procured from Thomas Baker Limited, Mumbai, India. Potassium trioxalatochromate(III) hydrate $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ (KTCR) was prepared by the method described in [21]. LTCR was prepared from solutions of LN and KTCR. 28 g of KTCR and 18 g of LN were dissolved separately in 100 mL of 1.2 M nitric acid. Both the solutions were cooled to 5°C and mixed together with vigorous stirring. After one minute green precipitate formed was separated, and washed with small portions of chilled 1.2 M nitric acid followed by washing with acetone. The compound was dried at room temperature over calcium chloride. The green compound formed was subjected to chemical analysis and assigned the formula $La[Cr(C_2O_4)_3]\cdot 9H_2O$. Water content of the compound was estimated using Karl Fischer method. Chromium was determined volumetrically after decomposing the samples with sulfuric acid followed by oxidation of Cr(III) to Cr(VI) with potassium perdisulfate. Oxalate was estimated volumetrically after removing lanthanum and chromium as their hydroxides. Lanthanum was estimated gravimetrically after coprecipitation as oxalate and volumetrically estimated chromium.

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### Synthesis of lanthanum chromite $LaCrO_3$

$LaCrO_3$ was prepared by heating LTCR in silicon carbide furnace as well as in microwave heating system. LTCR was heated in silicon carbide furnace at 900°C for one hour. In separate experiments, LTCR was heated in microwave heating system in the temperature range 400 to 900°C with an interval of 100°C for the same period. The product obtained after heat treatment at different temperatures was analysed by X-ray diffraction using the diffractometer, Siemens, Model D-500 at the scanning rate of $(2\theta=1°)$ $min^{-1}$, and wavelength of 0.15405 nm.

Surface area of $LaCrO_3$ prepared using the conventional and microwave heating techniques was measured by BET adsorption method.

### *Methods*

### Thermogravimetery (TG) and differential thermal analysis (DTA)

The TG curve of LTCR was recorded on 52.94 mg of sample in static air at the heating rate 10°C $min^{-1}$ using Mettler-Toledo TG instrument (Model-851). DTA plot for the decomposition of LTCR was recorded on 77.9 mg of sample in static air at the heating rate of 10°C $min^{-1}$, using the instrument supplied by Universal Thermal Analysis Instruments, Mumbai, built to our specifications.

## Results and discussion

The TG curve recorded for thermal decomposition of LTCR is shown in Fig. 1. The curve indicates that LTCR decomposes in four steps involving dehydration and decarboxylation to give $LaCrO_3$ as the final product. The sequence of decomposition steps could be expressed as

$$LaCr(C_2O_4)_3\cdot 9H_2O \rightarrow LaCr(C_2O_4)_3+9H_2O \quad (1)$$

$$8LaCr(C_2O_4)_3 \rightarrow 2La_2(CrO_4)_3+La_2O_3\cdot CO_2+2LaCrO_4+35CO+12CO_2 \quad (2)$$

$$2La_2(CrO_4)_3+La_2O_3\cdot CO_2+2LaCrO_4 \rightarrow 8LaCrO_4+CO_2+3/2O_2 \quad (3)$$

$$8LaCrO_4 \rightarrow 8LaCrO_3+4O_2 \quad (4)$$

The mass losses expected in each of the above decomposition steps were in good agreement with those calculated from the TG curve (Table 1). The formation of $LaCrO_4$ as a precursor (Eq. (3)) to $LaCrO_3$ could be confirmed from X-ray diffraction pattern of the product isolated at 650°C.

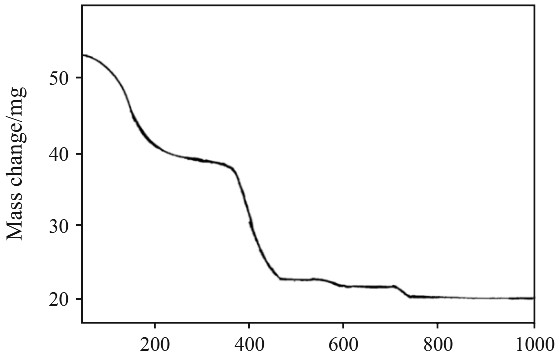


**Fig. 1** TG curve of LTCR recorded in static air

**Table 1** TG data on as dried precursor

| Steps | Temperature range/°C | Expected mass loss/% | Observed mass loss/% |
|---|---|---|---|
| I | RT–300 | 26.25 | 27.33 |
| II | 300–500 | 30.55 | 30.35 |
| III | 500–650 | 1.86 | 1.63 |
| IV | 650–800 | 2.59 | 2.87 |
| Total mass loss | | 61.25 | 62.18 |

The DTA curve of LTCR recorded in static air is presented in Fig. 2. The curve shows that LTCR decomposes in different steps involving dehydration and decarboxylation and yields final product at ~800°C. The first endothermic peak in DTA located around 150°C is due to dehydration. The endothermic peak is followed by two apparent exothermic peaks observed in the temperature range 300 to 500°C, which could have resulted due to decomposition of carboxylate group and simultaneous oxidation of evolved CO. The endothermic peak expected for the reaction expressed by Eq. (3) was too weak and merged in the background. A small endotherm was however observed ~800°C indicating the formation of $LaCrO_3$ from $LaCrO_4$ phase as concluded from the TG curve (Fig. 1). This information is useful in choosing the calcination temperature to get $LaCrO_3$ from LTCR, which could be below 800°C in the presence of microwave field.

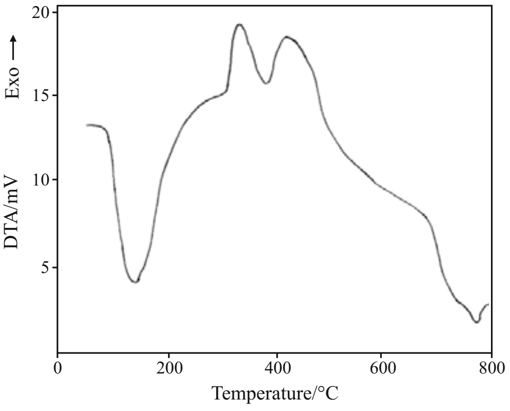


**Fig. 2** DTA curve of LTCR recorded in static air

*XRD patterns*

The X-ray diffraction patterns of LTCR calcined in silicon carbide furnace at 900°C and in microwave heating system at 400 and 500°C are shown in Fig. 3. XRD pattern of LTCR calcined in silicon carbide furnace at 900°C for one hour showed the formation of pure $LaCrO_3$. The XRD pattern suggests that $LaCrO_3$ formed is orthorhombic in nature and shows good agreement with that reported in the literature [15, 22, 23]. LTCR calcined in microwave heating system as low as at 500°C yielded the same product. The product formed after calcination of LTCR in microwave heating system in the temperature range 600 to 900°C was found to have the same structure but is more crystalline in nature. XRD pattern of LTCR calcined in microwave heating system at 400°C shows presence of some additional lines in $2\theta$ range 25 to 30° indicating that LTCR was not converted completely to $LaCrO_3$ at this temperature.

Scanning electron microscopic (SEM) image of the $LaCrO_3$ (in the pellet form) prepared by microwave heating technique at 500°C is presented in Fig.4. It shows that average particle size of $LaCrO_3$ formed is ~1.6 μm.

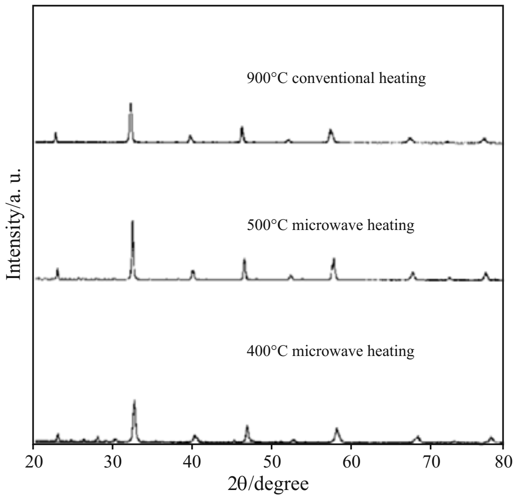


**Fig. 3** XRD pattern of LTCR calcined at various temperatures

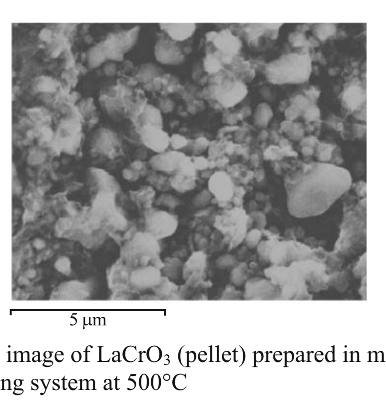


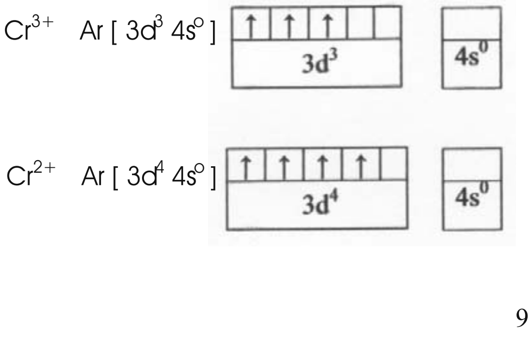
**Fig. 4** SEM image of $LaCrO_3$ (pellet) prepared in microwave heating system at 500°C

The surface area of the $LaCrO_3$ prepared in the present work, was measured by BET gas adsorption technique. Surface area of $LaCrO_3$ prepared by microwave and conventional heating techniques was found to be 2.8 and 1.2 $m^2\ g^{-1}$, respectively.

## Conclusions

Synthesis of $LaCrO_3$ reported by earlier investigators required high temperature (600–1000°C) and long heating period (4–12 h). We adopted a new method in which LTCR was heated at 900°C in silicon carbide furnace for one hour and in microwave heating system in the temperature range 400-900°C for the same period. It is observed that LTCR on heating in microwave system yielded pure orthorhombic $LaCrO_3$ at 500°C within one hour. On the contrary, to get the same product from LTCR applying conventional heating, processing temperature was relatively higher (900°C).

In the early years of research based on microwave processing of materials, it was assumed that the heating in microwave field was mainly dictated by the dielectric properties of the reactants. The materials with high dielectric loss (tanδ) interacted strongly with the microwave and facilitated rapid heating. In recent years, from the experiments performed in single mode microwave unit, it is proposed that both dielectric and magnetic properties of materials are involved in the interaction with the microwaves [24–26]. It has been observed in some cases that the materials which interact much strongly with magnetic field component showed poor interaction with the dielectric component of microwave field. The oxygen ion vacancies have been reported [27] to interact strongly with the microwaves and the magnetic properties conferred by the presence of unpaired electrons in *d* orbital of these elements could further enhance the microwave interaction, thereby facilitating the reaction at much lower temperature [28]. In the case of formation of $LaCrO_3$ from the LTCR precursor the lowering of average reaction temperature and enhancement of the reaction rate could be understood both in terms of formation of oxygen vacancies in $Cr_2O_3$ due to partial reduction of $Cr^{3+}$ to $Cr^{2+}$ by evolved CO during thermal decomposition (Eq. (2))



and the presence of unpaired electrons in ‘d’ orbitals in the Cr ions. The electronic configuration of unpaired electrons in ‘d’ orbitals can be represented as

Similar results obtained for the cobalt compound [13] indicated lower temperature of formation of $LaCoO_3$ (400°C) in microwave field.

It can be concluded from the present work that the microwave assisted technique adopted for the synthesis of $LaCrO_3$ is superior compared to the other methods, from the point of view of energy and time saving. Also the surface area of the $LaCrO_3$ formed employing microwave heating technique is more as compared to conventional heating technique.

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