SYNTHESIS OF La(Ca)CrO$_3$ POWDER BY AN AUTOIGNITION PROCESS AND STUDY OF ITS SINTERING BEHAVIOUR AND ELECTRICAL CONDUCTIVITY

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ABSTRACT

Ultrafine powders of calcium substituted lanthanum chromite has been synthesized by a simple process of autoignition of citrate-nitrate gel followed by calcination of the ash in the temperature range 600-650°C. Average particle size can be varied between 0.38 to 1.2μm through changes in the experimental parameters. These powders can be sintered at relatively low temperatures (1250-1300°C) compared to those normally reported. In addition, Bi$_2$O$_3$ is found to act as an effective sintering aid for this material. Sintered samples have been characterized in terms of their microstructure and electrical conductivity.

INTRODUCTION

Lanthanum chromite substituted with alkaline earth metals (Ca or Sr) have been widely accepted as the candidate for interconnection material in present generation Solid Oxide Fuel Cells (SOFCs). It satisfies most of the requirements of SOFC such as high electronic but negligible ionic conductivity, chemical stability in both oxidizing and reducing atmospheres, high density as well as chemical and thermo-mechanical compatibility with other cell components under operating conditions. However, it is rather difficult to process this material under conditions compatible with other cell components as its sintering temperature is relatively high, particularly in an oxidizing atmosphere. The sintering is also difficult due to appreciable volatization loss of chromium oxide at high temperatures in oxidizing atmosphere (1).

Several workers have attempted to improve the sinterability of LaCrO$_3$ powder by adopting different methods, e.g., preparing highly reactive powder (2), introducing nonstoichiometry (3-5), adding dopants or sintering aids (6-10) as well as by different processing techniques (11-13). As the reactivity of a ceramic powder depends largely on its particle size, an attempt has been made in this investigation to prepare ultrafine powders of pure and calcia
substituted LaCrO$_3$ by autoignition of citrate-nitrate gel, a process which has been found very effective by the present authors particularly to prepare Sr- and Ba-substituted LaMnO$_3$ powder suitable as the cathode material in SOFCs (14-17). LaCrO$_3$ is usually substituted either with calcium or strontium to obtain required properties of an interconnection material in SOFC. It has been observed earlier that Ca-substituted specimens can be sintered at lower temperatures compared to Sr-substituted ones (13). Therefore, in this investigation Ca-substituted (30 atom%) LaCrO$_3$ has been chosen for further investigation. Particle size of the powder has been varied by changing the preparation conditions. Since undoped LaCrO$_3$ is not used in SOFC, the effect of Bi$_2$O$_3$ as the sintering aid has been studied only with Ca-substituted LaCrO$_3$ powder. Finally the electrical conductivity of the sintered pellets has been measured at temperatures up to 1000°C to see its suitability in SOFC application.

EXPERIMENTAL

The powders have been synthesized by autoignition of dried citrate-nitrate gel, a process which has been successfully used by the present authors to prepare several complex oxides (14-20). The starting materials were analytical reagent grade lanthanum nitrate, calcium nitrate, chromium nitrate and citric acid. Several batches were prepared with variation in the ratio of reducing group (citrate) to oxidizing group (nitrate). Aqueous solution of citric acid was added to the mixed solution of metal nitrates so as to get a wide range of citrate : nitrate ratio in the precursor mixture. The compounds prepared were LaCrO$_3$ and La$_{0.7}$Ca$_{0.3}$CrO$_3$. The clear citrate-nitrate mixed solution was evaporated to dryness on a hot plate at a temperature of 90-95°C with continuous stirring. No precipitation was observed throughout the evaporation process. When the solution became highly viscous, stirring was stopped but heating continued. The viscous liquid formed into a transparent greenish gel which on further heating swelled with evolution of a large amount of gases and finally burnt with glowing flints. The combustion process took place in two distinct steps, the first one being relatively slow than the second one. Both combustion steps were complete within a few seconds giving rise to a greenish or yellowish (depending on the composition) colored ash which on calcination at 600-650°C yielded the desired powder.

Thermal decomposition of the gel was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in Shimadzu TGA-50 and DTA-50 units respectively at a heating rate of 10°C/minute in static air. Phase analysis of the powder was carried out using X-ray diffraction analysis (XRD) in Philips PW1750 diffractometer with...
CuK$_\alpha$ radiation. Particle size analysis was done in Micromeritics Sedigraph (Model 5100) unit.

The powder of 30 atom% Ca-substituted LaCrO$_3$ with and without addition of Bi$_2$O$_3$ as the sintering aid was pelletized at a pressure of 226MPa. Bi$_2$O$_3$ powder was mixed with this powder by wet milling for 12hrs using butanol as the mixing medium. The amount of Bi$_2$O$_3$ addition was varied from 1-15wt% . The pellets were sintered in an electrically heated furnace in the temperature range of 1250-1350°C for a soaking period of 6hrs in air. The sintered densities were measured by liquid displacement method. The fractured surfaces of the sintered pellets were observed under scanning electron microscope (Stereo Scan S-250, USA). Electrical conductivity of the sintered specimens was measured in the range room temperature to 1000°C by four probe technique using H.P. multimeter (Model 3458A).

**RESULTS AND DISCUSSION**

Thermal analysis of the dried gel of different batches has been carried out up to a temperature of 1000°C. The representative TGA and DTA curves of the gel corresponding to 30 atom% Ca-substituted LaCrO$_3$ are shown in Fig.1. It may be noted from the TGA curve that the weight loss takes place in two distinct steps and the major loss taking place during the first step, which however, does not correspond to the autocombustion reaction as evident from the very small DTA peak indicating a relatively low enthalpy change (251 Joule/gm) during the step. In contrast, a very sharp DTA peak arising from a very high enthalpy change (915 Joule/gm) for the second decomposition step indicates that the intermediate compound resulting from the first stage of the reaction undergoes a combustion type reaction. Once the combustion process is over, the temperature comes down quickly to the normal condition. The large difference (60°C) between the on-set of second stage reaction at 360°C and the peak temperature of 420°C indicates a self propagating combustion process identical to those observed earlier in a few other systems of this kind using different combustible species (14-17). An insignificant weight loss (less than 4%) above 374°C indicates that the formation of LaCrO$_3$ phase is nearly complete during the autocombustion process and there is no appreciable formation of metallic carbonates.

X-ray diffraction pattern of the ash (Ca-substituted composition) obtained from autocombustion indicates that the powder is mostly amorphous with very little crystallinity (Fig. 2(a)). This powder when calcined at 650°C shows well-crystalline LaCrO$_3$ in association with a small amount of CaCrO$_4$ (Fig. 2(b)). Similar contamination has also been observed in powders prepared by some other routes (4). It may, however, be noted that sintering at 1300°C eliminates this impurity
phase (Fig. 2(c)) and leads to the formation of a single phase LaCrO$_3$ material. We believe that the minor phase (CaCrO$_4$) goes into solid solution during high temperature sintering. It has, however, been reported that the presence of this phase enhances liquid phase sintering at higher temperatures (5).

The vigour of the auto combustion reaction and consequently the particle size of the powder and also the distribution can be varied by changing the initial citrate : nitrate ratio in the solution. Median diameter ($D_{50}$) of the Ca-substituted powder prepared with different citrate-nitrate ratio is given in Table-I. The minimum particle size of the unsubstituted powder (calcined at 650°C) which could be achieved in this investigation for citrate-nitrate ratio of 2.5 is 0.38μm and the same value for the 30 at% Ca-substituted LaCrO$_3$ powder is 0.57μm. The complete size distribution of these powders are presented in Fig. 3.

Ca-substituted LaCrO$_3$ powder with particle size of 0.57μm has been sintered in air at temperatures 1250, 1300 and 1350°C for a soaking period of 6hrs with and without addition of Bi$_2$O$_3$ as a sintering aid. Within the temperature range 1250-1350°C, as the best result is obtained at 1300°C, sintered density data for the specimens for both with and without Bi$_2$O$_3$ and sintered at 1300°C for 6hrs are given in Table-II. The density achieved is 85-87% of the theoretical value for the specimens without addition of Bi$_2$O$_3$, the SEM photographs of the fractured surfaces of which are shown in Figs. 4(a,b). It has been observed that change of sintering temperature within the range investigated has very little effect on the extent of densification. But with the addition of 10 wt % Bi$_2$O$_3$ as the sintering aid the density increases to 95-96 % of theoretical value when sintered in the same temperature range (1250-1350°C). The corresponding microstructures are shown in Figs. 4(c,d). A very similar effect of Bi$_2$O$_3$ on the densification of La(Sr)MnO$_3$ cathode material was earlier observed by the present authors (17). As in the previous case, the XRD pattern of the present samples sintered with addition of 10 wt% Bi$_2$O$_3$ does not show any second phase containing bismuth. Presence of any glassy (or liquid) phase along the grain boundaries is also not clearly visible from the SEM photographs. The exact role of this sintering aid is still to be investigated. The average grain size of most of the sintered samples as observed by SEM is $\approx$ 0.8μm and therefore the present material is relatively a fine grained product compared to those reported earlier (8).

Electrical conductivity of the sintered samples of Ca-substituted LaCrO$_3$ both with and without the addition of the sintering aid has been measured in the range room temperature to 1000°C. It is observed
that \( \text{Bi}_2\text{O}_3 \) addition improves the electrical conductivity to an appreciable extent. The plausible reason is the enhancement of sintered density due to bismuth addition. At 1000°C, the conductivity of \( \text{Bi}_2\text{O}_3 \) containing sample is about 27 S/cm compared to 12 S/cm for the sample without containing bismuth. This conductivity is slightly lower than that observed by Nasrallah et al. (8) possibly because of the wide difference in grain sizes of the samples in two cases. The grain size of their samples was about 5µm compared to less than 1µm in our case. So the grain boundary area and consequently the grain boundary resistance is significantly large in our samples and this may be the reason for lower value of conductivity. Further work is in progress to confirm this view.

CONCLUSION

Ultrafine powders of pure and Ca-substituted \( \text{LaCrO}_3 \) have been prepared by autoignition of citrate-nitrate gel and has been sintered to about 87% of theoretical density at 1300°C. However, addition of \( \text{Bi}_2\text{O}_3 \) (10 wt%) improves the density to around 96%. Preliminary electrical measurements indicate that electrical conductivity of the material is significantly lower than those reported in the literature, which is possibly due to its finer grain size.

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Table-I: Change of median diameter ($D_{50}$) of Ca-substituted LaCrO$_3$ with citrate-nitrate ratio

| Citrate:Nitrate | Median Diameter ($D_{50}$) (μm) |
|-----------------|---------------------------------|
| 1.00            | 1.10                            |
| 2.00            | 0.80                            |
| 2.50            | 0.57                            |
| 3.00            | 1.00                            |
| 4.00            | 1.20                            |

Table-II: Percentage theoretical density of Ca-substituted LaCrO$_3$ sintered at 1300°C for 6hrs.

| wt% $\text{Bi}_2\text{O}_3$ | % of theoretical density |
|-----------------------------|---------------------------|
| 0                           | 86.6                      |
| 2.5                         | 89.0                      |
| 5.0                         | 92.4                      |
| 7.5                         | 95.0                      |
| 10.0                        | 96.4                      |
| 12.5                        | 92.0                      |
Fig. 1: DTA and TGA of dried gel for 30 atom% Ca-substituted LaCrO$_3$ at a heating rate of 10°C/min.

Fig. 2: XRD pattern of 30 atom% Ca-substituted LaCrO$_3$ (a) ash after ignition (b) powder calcined at 650°C and (c) pellet sintered at 1300°C.

Fig. 3: Particle size distribution of the calcined power of pure and 30 atom% Ca-substituted LaCrO$_3$. 

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Mass Finer (µm) - Wt.loss (%) / Temp.diff. (°C)

Fig. 2: XRD pattern of 30 atom% Ca-substituted LaCrO$_3$ (a) ash after ignition (b) powder calcined at 650°C and (c) pellet sintered at 1300°C.
Fig. 4: SEM fractograph of 30 atom% Ca-substituted LaCrO$_3$ sintered without addition of Bi$_2$O$_3$ at (a) 1250°C / 6 hrs., (b) 1300°C / 6 hrs. and with addition of Bi$_2$O$_3$ (10 wt%) at (c) 1250°C / 6 hrs., (d) 1300°C / 6 hrs.