JOURNAL OF Materials CHEMISTRY

Hydrothermal synthesis and characterization of $LaCrO_3$

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Received 2nd June 1999, Accepted 30th June 1999

The synthesis of perovskite-type $LaCrO_3$ under mild hydrothermal conditions is reported. The synthesized product was characterized by means of XRD, IR, SEM and elemental analysis. The results indicated that the phase corresponded to orthorhombic perovskite-type $LaCrO_3$, and the product had a narrow particle size distribution in the range of 1–3 μm. The effect of hydrothermal conditions on the synthesis of $LaCrO_3$ was investigated. Under the hydrothermal conditions used, the optimum crystallization temperature was 240–260 °C. For the formation of pure $LaCrO_3$, a higher alkalinity ($\geqslant 8$ mol dm^{-3} KOH) is necessary because Cr^{3+} is significantly amphoteric. In the reactant mixing process, the optimum stirring time is 5–10 min because of the oxidation of CrO_2^- ion by oxygen in the air. CrO_4^{2-} does not show significant hydrothermal reactivity under the present conditions.

1 Introduction

High-temperature solid oxide fuel cells (SOFC) have been extensively investigated for the last two decades because of their potential use as clean and efficient power-generating devices. Alkaline earth metal substituted lanthanum chromates are known to be very promising interconnecting materials for SOFCs based on stabilized zirconia electrolytes.[1] However, $LaCrO_3$-based materials have poor sinterability because of their extremely refractory nature and higher volatility in oxidative atmosphere at elevated temperatures.[2] Many attempts have been made to obtain dense materials of $LaCrO_3$-based oxides, such as by using additives, *etc.*[3,4] The additives are able to decrease the sintering temperature, but possible separation of small amounts of additional phases imposes certain limitations on the use of $LaCrO_3$-based materials.[5] For this reason, it is important to prepare $LaCrO_3$-based materials at lower temperatures. Recently, several preparation techniques based on solution chemistry methods, such as the citrate gel process,[6] a co-precipitation technique[5] and a complex compound process[2] have been employed.

Oxide powder, of high purity, narrow particle size distribution, high phase homogeneity, controlled particle morphology and high degree of crystallinity can be produced *via* hydrothermal processes. $LaCrO_3$-based materials have been prepared hydrothermally at 350–450 °C,[7] but the influence of the hydrothermal conditions was not described in detail. Here, we have synthesized $LaCrO_3$ hydrothermally under more mild conditions, and have optimised the conditions.

2 Experimental

In the hydrothermal synthesis of $LaCrO_3$, freshly prepared $La_2O_3 \cdot xH_2O$ was used as the lanthanum source. $La_2O_3 \cdot xH_2O$ was prepared by adding NH_3 (aq) to an $La(NO_3)_3$ aqueous solution resulting in a white precipitate which was washed with de-ionized water and dried at 90 °C. The La_2O_3 content of this precipitate was measured by TG. The hydrothermal synthesis of $LaCrO_3$ was carried out in a stainless steel autoclave with a Teflon liner (*ca.* 20 cm^3 capacity) under autogenous pressure. The typical synthesis procedure is as follows: a 0.2–0.3 mol dm^{-3} $CrCl_3$ solution was prepared in de-ionized water, and the other reactants were added to the solution in sequence $La_2O_3 \cdot xH_2O$ followed by KOH to obtain a slurry with a molar composition $CrO_{1.5}:LaO_{1.5}:KOH = 1\text{–}1.1:1:10\text{–}80$. The slurry was transferred into an autoclave and heated at 260 °C for 7 days. After cooling, the product was filtered off, washed with dilute acetic acid and de-ionized water, and dried at ambient temperature.

X-Ray diffraction patterns were acquired from a Rigaku D/MAX-IIIA powder diffractometer with a nickel-filtered Cu-Kα (1.5418 Å) source. The IR spectrum was measured with a Nicolet 5DX-FT infrared spectrophotometer. The particle size and morphology were investigated by SEM using a Hitachi X-156 scanning electron microscope. Elemental analysis was carried out on the acidified filtrate using a Leeman Labs Plasma-Spec (I)-AES. Differential thermal analysis and thermogravimetry (DTA–TG) of $La_2O_3 \cdot xH_2O$ were carried out using a Perkin-Elmer TG-7 thermal analyzer and DTA-700. Samples were heated from 25 to 1000 °C at a heating rate of 10 °C min^{-1} with an air flow of 5 cm^3 min^{-1}.

3 Results and discussion

3.1 XRD, SEM and IR analysis

The X-ray diffraction pattern of $LaCrO_3$ powder processed at 260 °C in 8.5 mol dm^{-3} KOH for 7 days is shown in Fig. 1. A perovskite-type $LaCrO_3$ phase is formed free of impurity phases and with a high degree of crystallinity. Based on X-ray diffraction data, $LaCrO_3$ crystallized in the orthorhombic space group *Pbnm*[8] with unit cell parameters $a = 5.484$, $b = 5.524$, and $c = 7.767$ Å. The filtrate following hydrothermal synthesis was subjected to elemental analysis for La^{3+} and Cr^{3+}. When the Cr/La ratio in the initial solute is > 1.05, it is observed that lanthanum is reacted completely (XRD and ICP measurements) and the Cr/La ratio of the product is close to stoichiometric for $LaCrO_3$.

Fig. 2 shows the morphology of $LaCrO_3$ according to SEM. The $LaCrO_3$ crystals have a cubic crystal habit and a small particle size range of 1–3 μm. The IR spectrum of $LaCrO_3$ powder (Fig. 3) shows two strong absorption bands around 430 and 610 cm^{-1} which can be assigned to O–Cr–O deformation and Cr–O stretching vibrations, respectively.[9]

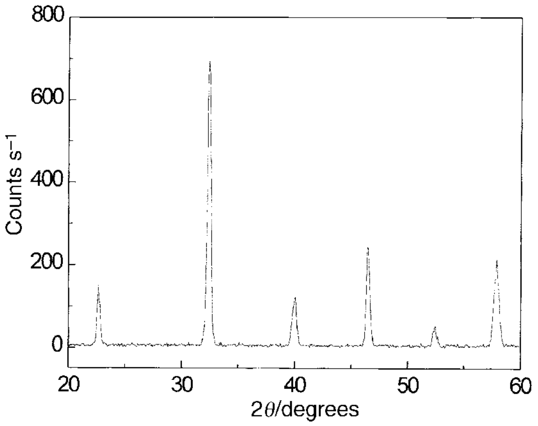

Fig. 1 X-Ray powder diffraction pattern of $LaCrO_3$ processed in 8 mol dm^{-3} KOH at 260 °C for 7 days.

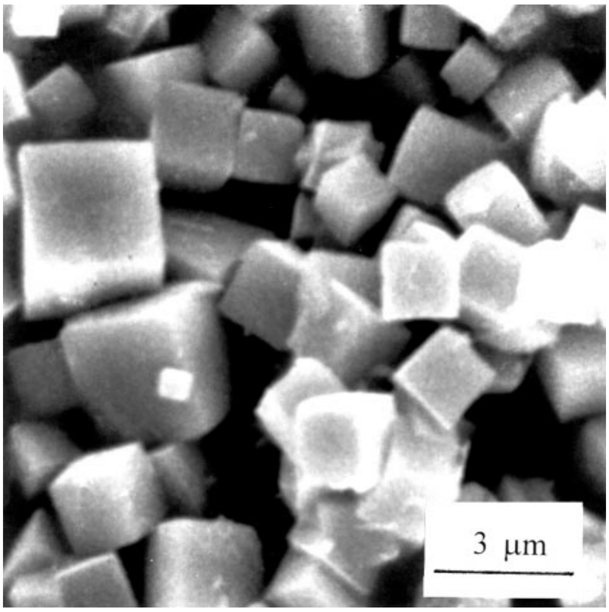

Fig. 2 SEM photograph of $LaCrO_3$.

3.2 Effect of crystallization temperature

Fixing the alkalinity, reaction and stirring times to 8.5 mol dm^{-3} KOH, 7 days and 10 min, respectively, the effect of temperature on the synthesis of $LaCrO_3$ was investigated. The formation of $LaCrO_3$ was observed by XRD. As shown in Fig. 4, a qualitative estimate of the crystallinity of the products obtained at different temperatures is estimated by monitoring the intensity of the 100% intensity reflection of $LaCrO_3$, with the product synthesized at 280 °C regarded as 100% crystalline. In the experiments, the lowest temperature at which $LaCrO_3$ was formed was 120 °C with hexagonal La_2O_3 of low crystallinity only observed after the initial solute was heated to 100 °C for 7 days. In the temperature range 120–220 °C, the crystallinity is increased significantly with increasing temperature while the crystallinity increase is less marked in the temperature range 220–280 °C.

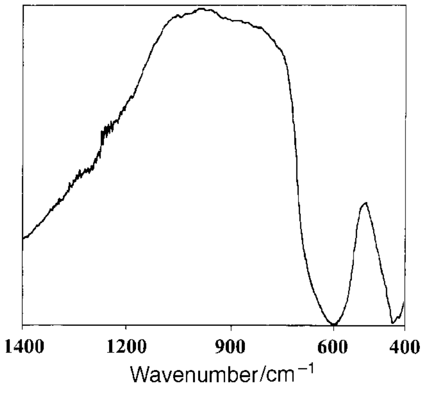

Fig. 3 IR spectrum of $LaCrO_3$.

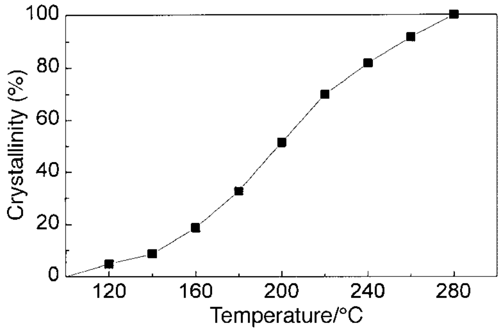

Fig. 4 Influence of crystallization temperature on the crystallinity of $LaCrO_3$ processed in 8 mol dm^{-3} KOH for 7 days.

These observations indicate that the growth and recrystallization speeds of $LaCrO_3$ crystals are increased with increasing temperature. In terms of $La(OH)_3$, lower temperatures may be advantageous to the crystallization of $LaCrO_3$ since the solubility of $La(OH)_3$ is decreased at higher temperatures.[10] However, experimental results indicated that the crystallinity of $LaCrO_3$ was poor at lower crystallization temperatures. While the solubility of $La(OH)_3$ is reduced to some extent at higher temperatures, the growth and the recrystallization speeds of $LaCrO_3$ are increased significantly. Therefore, higher crystallization temperatures favor the crystallization process of $LaCrO_3$ crystals.

For some advanced applications of $LaCrO_3$-based materials, using temperatures above 280 °C is not necessary because generally ceramic forms of the materials are used. In addition, Teflon liners can not be used above 280 °C. As a consequence the optimum crystallization temperature is *ca.* 240–260 °C for the synthesis of $LaCrO_3$-based materials powders.

3.3 Effect of alkalinity

The effect of alkalinity on the hydrothermal synthesis of $LaCrO_3$ was investigated when alkalinity was varied between 2–16 mol dm^{-3} KOH (KOH/Cr = 10–80), with temperature and reaction and stirring times fixed at 260 °C, 7 days and 10 min, respectively, and results are given in Table 1. No $LaCrO_3$ formed below 6 mol dm^{-3} KOH, with La_2O_3 and CrOOH detected as the main phases in the products. However, it was observed that some La_2O_3 remained in the products when the alkalinity was > 10 mol dm^{-3} KOH.

This suggests that the effect of alkalinity is associated with the perovskite-type structure and the properties of Cr^{3+} ions. The ABO_3 type perovskite structure can be described as a framework of corner-shared BO_6 octahedra that contains A-cations in 12-coordinate sites. Therefore, the hydrothermal activity of B-cations significantly influences the hydrothermal synthesis of perovskite-type oxides. It is an essential prere-

Table 1 Influence of alkalinity on the hydrothermal synthesis of $LaCrO_3$

KOH concentration/mol dm^{-3}	Reaction products (XRD)
6	$La(OH)_3$, CrOOH, Cr_2O_3
8	$LaCrO_3$
9	$LaCrO_3$
10	$LaCrO_3$, $La(OH)_3$
12	$LaCrO_3$, $La(OH)_3$

quisite to obtain perovskite-type oxides that the hydroxy-complex of the B-cation condenses *via* dehydration in alkaline medium. The hydroxy-complex of the B-cation, being more amphoteric, condenses less readily than that of A at a given alkalinity because the complex is more stable. A high alkalinity is thus required when the B-cation shows significant amphoterism as is true for Cr^{3+}. Here formation of pure $LaCrO_3$ requires $\geqslant 8$ mol dm^{-3} KOH medium.

Besides amphoterism, Cr^{3+} ions also show reducing properties to a certain extent in alkaline media. The fact that the hydrothermal synthesis of $LaCrO_3$ has a narrow optimum alkalinity (8–10 mol dm^{-3}) may be explained by this reducing property. The reaction of CrO_2^- ion as a reductant can be expressed by eqn. (1):[10]

$$CrO_4^{2-} + 2H_2O + 3e^- \leftrightharpoons CrO_2^- + 4OH^- \quad E^\circ_{298\,K} = -0.13\ V \tag{1}$$

where CrO_2^- is a simplified representation of the $Cr(OH)_6^{3-}$ hydroxy-complex.[10] In the present hydrothermal system, O_2 can act as an oxidant, and shows the following reduction reaction [eqn. (2)].[10]

$$O_2 + 2H_2O + 4e^- \leftrightharpoons 4OH^- \quad E^\circ_{298\,K} = -0.401\ V \tag{2}$$

At room temperature, the reaction of O_2 with CrO_2^- is thermodynamically favored given the large difference of standard electrode potentials ($E^\circ_{\text{eqn. (2)}} - E^\circ_{\text{eqn. (1)}} = 0.531$ V). However, at room temperature, CrO_2^- is generally oxidized using stronger oxidants, such as H_2O_2.[10] Given that the autoclave is *ca.* 80% filled, the amount of oxygen in the hydrothermal system is *ca.* 3.27×10^{-5} mol, according to the ideal gas law. According to eqns. (1) and (2), three and four electrons are involved, respectively, and thus 4.36×10^{-5} mol CrO_2^- can be oxidized in the synthesis process, which is *ca.* 0.9–1.3 mol% of the total Cr^{3+} ions in the solute. Oxidization of CrO_2^- ions was supported by the nature of the filtrates. After synthesis, the filtrates show the characteristic yellow color of CrO_4^{2-} ions when the alkalinity is >10 mol dm^{-3} KOH. Additionally the filtrates were subjected to a test for CrO_4^{2-} using $Pb(NO_3)_2$ for which a yellow $PbCrO_4$ precipitate was formed. However, oxidation of CrO_2^- ions during the crystallization process does not satisfactorily explain the presence of La_2O_3 when the alkalinity is >10 mol dm^{-3} KOH. Oxidization of CrO_2^- ions by oxygen in the air is thus likely according to eqns. (1) and (2), and the oxido–reduction of CrO_2^- ion with O_2 is expressed by eqn. (3).

$$4CrO_2^- + 3O_2 + 4OH^- \leftrightharpoons 4CrO_4^{2-} + 2H_2O \tag{3}$$

This reaction is favored by increased alkalinity. For this reason, the influences of stirring time and Cr/La ratio on the hydrothermal synthesis of $LaCrO_3$ were investigated.

The effect of stirring time was investigated in the range 5–20 min. In this test, alkalinity, Cr/La ratio, reaction time and temperature were fixed at 12 mol dm^{-3} KOH, 1 : 1, 7 days and 260 °C, respectively. In order to significantly observe oxidation of CrO_2^-, the alkalinity and Cr/La ratio were changed from 8.5 mol dm^{-3} KOH and 1.1 to 12 mol dm^{-3} KOH and 1, respectively. As shown in Fig. 5, pure $LaCrO_3$ was observed only when the stirring time was 5 min. At times >5 min, La_2O_3 was present, and the intensities of its XRD reflections were enhanced with increased stirring times; *i.e.* the oxidation of CrO_2^- ions is increased with the increase of stirring time. Therefore, it is clear that CrO_2^- ions are oxidized partially by oxygen in the air during the reactant mixing process. For the synthesis of $LaCrO_3$, the raw solute was stirred for only 3–5 min to ensure its homogeneity. Even under these conditions oxidation of CrO_2^- ions occurs to some extent. However, La_2O_3 remaining in the product was not detected when the stirring time is 5 min. This is likely to be associated with the formation of $LaCrO_3$ and the characteristics of the perovskite-type structure. In formation of $LaCrO_3$, the equilibrium of eqn. (3) shifts to the left to a certain extent, but this is not very significant since La_2O_3 is observed in the product when stirring time is >5 min. On the other hand, defects are generally readily accommodated within the perovskite-type structure; it can be postulated that CrO_4^{2-} ions may occupy B-sites to an extent instead of Cr^{3+} ions. However, the B-site requires an octahedral six-coordinate ion, whereas CrO_4^{2-} has a tetrahedral structure. For such a substitution in which a large distortion is introduced into the $LaCrO_3$ crystal lattice, a high activation energy is required. However, under the present hydrothermal conditions, the supplied energy is modest owing to the low crystallization temperature. Thus CrO_4^{2-} substitution for B-site Cr^{3+} ion is likely to be insignificant. For this reason, the controlled stirring process is one of the key points for the synthesis of $LaCrO_3$.

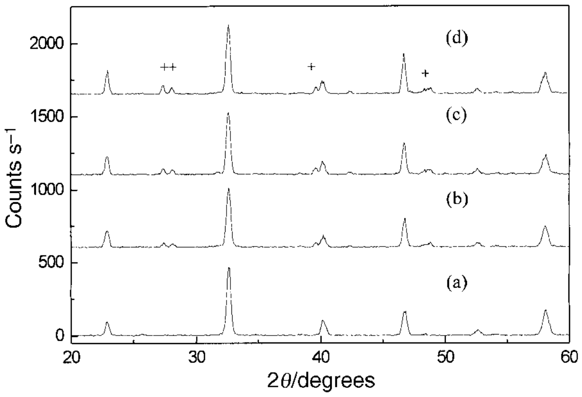

Fig. 5 Influence of stirring time on the hydrothermal synthesis of $LaCrO_3$; + represents La_2O_3.

In order to confirm further the influence of the oxidation of CrO_2^- in the stirring process, the effect of Cr/La ratio was investigated and was within the range 1 : 1–1.2 : 1, and the stirring time was fixed at 20 min. The other conditions were similar to the stirring time experiments. We found that pure $LaCrO_3$ can form only when Cr/La = 1.2, and the amount of La_2O_3 formed increased with a decrease in the Cr/La ratio. In the mixing process, CrO_2^- ion can be oxidized partially, but a high enough CrO_2^- concentration ensures that the Cr/La ratio in the reactive system will be close to the stoichiometry of $LaCrO_3$. The reducing property of Cr^{3+} ion means that La_2O_3 remains when the alkalinity is >10 mol dm^{-3} KOH.

In the present work, CrO_4^{2-} ion was not incorporated into any of the solid products (XRD analysis), probably owing to the high activation energy required for its incorporation into a perovskite type structure.

4 Conclusions

The synthesis of $LaCrO_3$ has been shown to be feasible under mild hydrothermal conditions. In this work, the optimum crystallization temperature was 240–260 °C. Since Cr^{3+} shows significant amphoterism, a high alkalinity ($\geqslant 8$ mol dm^{-3} KOH) is necessary to obtain pure $LaCrO_3$. In mixing the reagents, the optimum stirring time is 5–10 min owing to oxidation of CrO_2^- ion by oxygen in the air. CrO_4^{2-} ion does not show significant hydrothermal reactivity under the present conditions.

Acknowledgements

This work was partially supported by the National Science Foundation of China.

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Paper 9/04399C