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RARE-EARTH CHROMIUM CITRATES AS PRECURSORS FOR RARE-EARTH CHROMITES: LANTHANUM BISCITRATO CHROMIUM(III) DIHYDRATE, $La[Cr(C_6H_5O_7)_2] \cdot 2H_2O$

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ABSTRACT

The thermal decomposition of lanthanum biscitrato chromium(III) dihydrate has been studied in static air and dynamic argon atmospheres. The complex decomposes in four steps: dehydration, decomposition of the citrate to an intermediate oxycarbonate, formation of $LaCrO_4$(V) from oxycarbonate, and finally decomposition of $LaCrO_4$(V) to $LaCrO_3$. Formation of $LaCrO_4$(V) requires the presence of oxygen.

The decomposition behaviour of a mechanical mixture of lanthanum citrate hydrate and chromium citrate hydrate was compared with that of the citrato complex. Both the starting material and the intermediates were characterized by X-ray diffraction, IR electronic and ESR spectroscopy, surface area and magnetic susceptibility measurements, as well as by chemical analysis. A scheme is proposed for the decomposition of lanthanum biscitrato chromium(III) dihydrate in air. $LaCrO_3$ can be obtained at temperatures as low as 875 K by isothermal decomposition of the complex.

INTRODUCTION

We have been investigating low-temperature chemical methods for the preparation of technologically useful oxide perovskites. Oxalato complexes have been employed for the preparation of titanates [1–4] and zirconates [5–7] of alkaline earths and lead, as have rare-earth cobaltites [8]. Citrate complexes could be promising precursors for the low-temperature preparation of rare-earth transition metal perovskite oxides. Of late there has been renewed interest in polycrystalline lanthanum chromite, because of its oxidation resistance, electronic conduction and highly refractory nature [9–11]. The major applications of lanthanum chromite are as hot electrodes for MHD power generation [12] and as a promising fuel cell electrode [13].

There have been a couple of reports [14,15] on the preparation of lanthanum chromite through a citrate precursor, but the precursor has not been well characterized, and has been of variable stoichiometry. The present work deals with the preparation, characterization and thermal decomposi-

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tion of lanthanum biscitrato chromium(III) dihydrate (LCC), leading to the formation of chemically pure, fine-grained, stoichiometric lanthanum chromite.

EXPERIMENTAL

Reagents

All the reagents used were either AnalaR grade or of higher purity. 99.99% lanthanum oxide, AAS standard from Alfa Products, Merck guaranteed reagent citric acid, and BDH AnalaR chromium nitrate were used.

Preparation

50 ml 0.02 M lanthanum nitrate and 50 ml 0.02 M chromium nitrate were mixed with 50 ml 0.04 M citric acid (mole ratio of La : Cr : citric acid = 1 : 1 : 2). The mixture was evaporated on a water bath at 353 K to a viscous liquid, which was later transferred to an evaporating dish. Further drying was carried out at 363 K in a vacuum of 10^{-1}–10^{-2} mmHg, for 6–18 h. This gave rise to a foamy residue of lanthanum biscitrato chromium(III) hydrate. The degree of hydration varied from 2 to 8 H_2O mol^{-1}. Drying at 363 K for 12 h in a vacuum of 10^{-2} mmHg produced the dihydrate which was used in the present investigation.

Lanthanum citrate tetrahydrate ($LaC_6H_5O_7 \cdot 4H_2O$) and chromium citrate nonahydrate ($CrC_6H_5O_7 \cdot 9H_2O$) were prepared by double decomposition of the nitrates of lanthanum and chromium, respectively, with the stoichiometric quantity of trisodium citrate solution. The precipitates were filtered, washed well and dried at ambient temperature.

Analysis

Lanthanum was estimated gravimetrically after double precipitation of its oxalate. Chromium was determined volumetrically, by decomposition of the complex with sulphuric acid, followed by oxidation of Cr(III) to Cr(VI) with potassium persulphate. Citrate content in the complex was computed from elemental analysis as well as by oxidation with ceric ammonium sulphate [16] in the presence of excess sulphuric acid.

Carbonate in the intermediate isolated during decomposition of the citrate complex was estimated by decomposing it with hydrochloric acid and absorbing the evolved CO_2 after drying in ascarite.

Thermograms were recorded using an Ulvac TA-1500 automatic thermal analyser, with a heating rate of 20 °C min^{-1}. IR spectra were recorded in both alkali halide pellets and Nujol mulls, using a Perkin–Elmer 597 spectrometer. X-ray diffractograms were recorded on a Philips PW 1050/70 diffractometer with a vertical goniometer, using Cu $K\alpha$ radiation and a scan rate of 2° $\min^{-1}$. Electron micrographs were obtained using a Cambridge Stereoscan 150 scanning electron microscope. Transmission micrographs and electron diffractions were obtained using a Philips EM 301 microscope. Electronic absorption spectra were recorded using a Hitachi UV–VIS recording spectrophotometer, with samples in the form of Nujol mulls between optical grade fused-quartz discs. Surface areas were determined by nitrogen adsorption using a Micromeritics Accusorb 2100E physical adsorption analyser. Particle sizes were estimated using a Granulometer 715E452. ESR spectra were recorded on a Varian X-band EPR spectrometer, Model E-109. Magnetic susceptibilities were measured using an EG and G Princeton Applied Research vibrating sample magnetometer, Model 155. Carbon and hydrogen analyses were carried out using a Carlo–Erba C–H–N–S–O automatic elemental analyser, model 1106.

RESULTS

Analysis of the complex gave La = 22.94%, Cr = 8.57%, citrate = 62.50% and $H_2O = 5.89\%$, which agreed well with the calculated values for $LaCr(C_6H_5O_7)_2 \cdot 2H_2O$ (La = 22.96%, Cr = 8.59%, citrate = 62.49% and $H_2O = 5.96\%$). The complex was a bluish-black non-hygroscopic foamy solid, which was insoluble in water as well as common organic solvents. It was amorphous to X-rays. The IR spectrum of the complex (Fig. 1 (b)) is less complex than that of citric acid (Fig. 1 (a)), but the absorption peaks are broad. The broad band in the region 3400–2900 cm^{-1} can be attributed to the O–H stretching vibration of the hydroxyl group of citrate, as it is also observed for the anhydrous complex. The broad and unresolved bands at 1565 and 1400 cm^{-1} are characteristic of completely ionized carboxyl groups with equalized C–O bonds. No bands attributable to free citric acid (1710 cm^{-1}) or ionic nitrate (1385 cm^{-1}) impurity appear in the spectrum [17].

The LCC consisted of porous irregular particles which were agglomerates of around 40 μm in size, as shown in the scanning electron micrographs (Figs. 2a and 2b). Particle size analysis also gives a mean particle diameter of ~ 40 μm.

The electronic spectrum of the solid consists of a sharp band at 36630 cm^{-1}, which can be assigned to the charge-transfer process. The ESR spectrum (not shown) at room temperature (300 K) as well as at 77 K gives a very broad signal with a g value of 1.94, which is slightly less than the value expected for Cr^{3+} in an octahedral field. This probably indicates a distortion from octahedral symmetry [18].

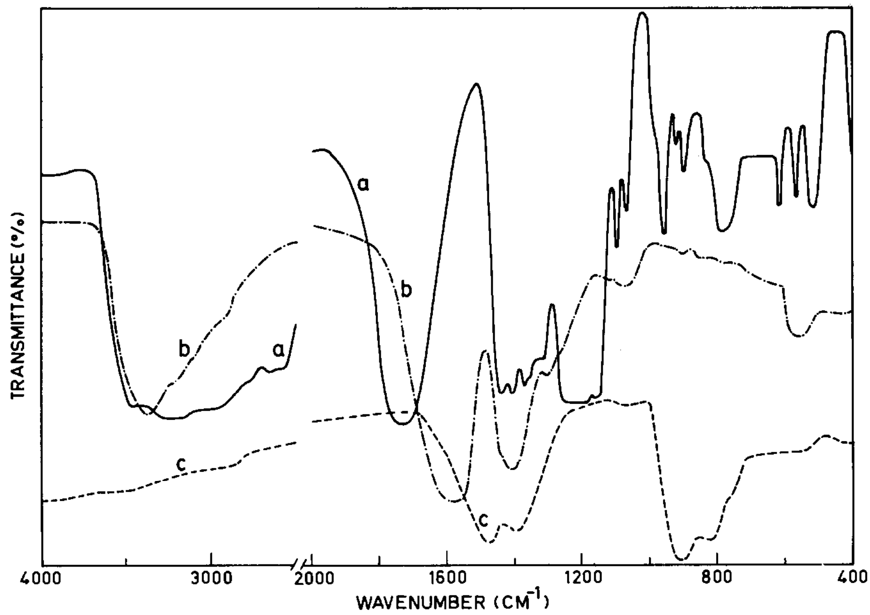

Fig. 1. IR spectra of: (a) citric acid; (b) LCC; (c) $LaCrO_{3-x}(CO_3)_x$.

The available evidence indicates that citrate coordinates to the chromium through carbonyl groups, giving rise to a distorted octahedral geometry. The hydroxyl groups are not involved in coordination.

Thermal decomposition of LCC

Thermograms in static air and dynamic argon atmospheres are shown in Fig. 3. The decomposition was found to proceed through various steps. At least four steps could be identified from the TG curves. The probable reactions are: (i) dehydration; (ii) decomposition of the anhydrous citrate complex to produce an oxycarbonate; (iii) decomposition of the oxycarbonate to lanthanum chromate(V); and (iv) decomposition of chromate(V) to lanthanum chromite(III).

Dehydration

LCC was found to undergo dehydration up to 400 K with a weight loss of around 6%, against the calculated 5.95% corresponding to the loss of $2H_2O$ mol^{-1}. This dehydration appears as an endotherm on the DTA curve.

Decomposition of anhydrous citrate

This was found to be the most important and at the same time the most complex stage of decomposition. The citrate is probably converted to acotinate and then subjected to decarboxylation. This process was found to

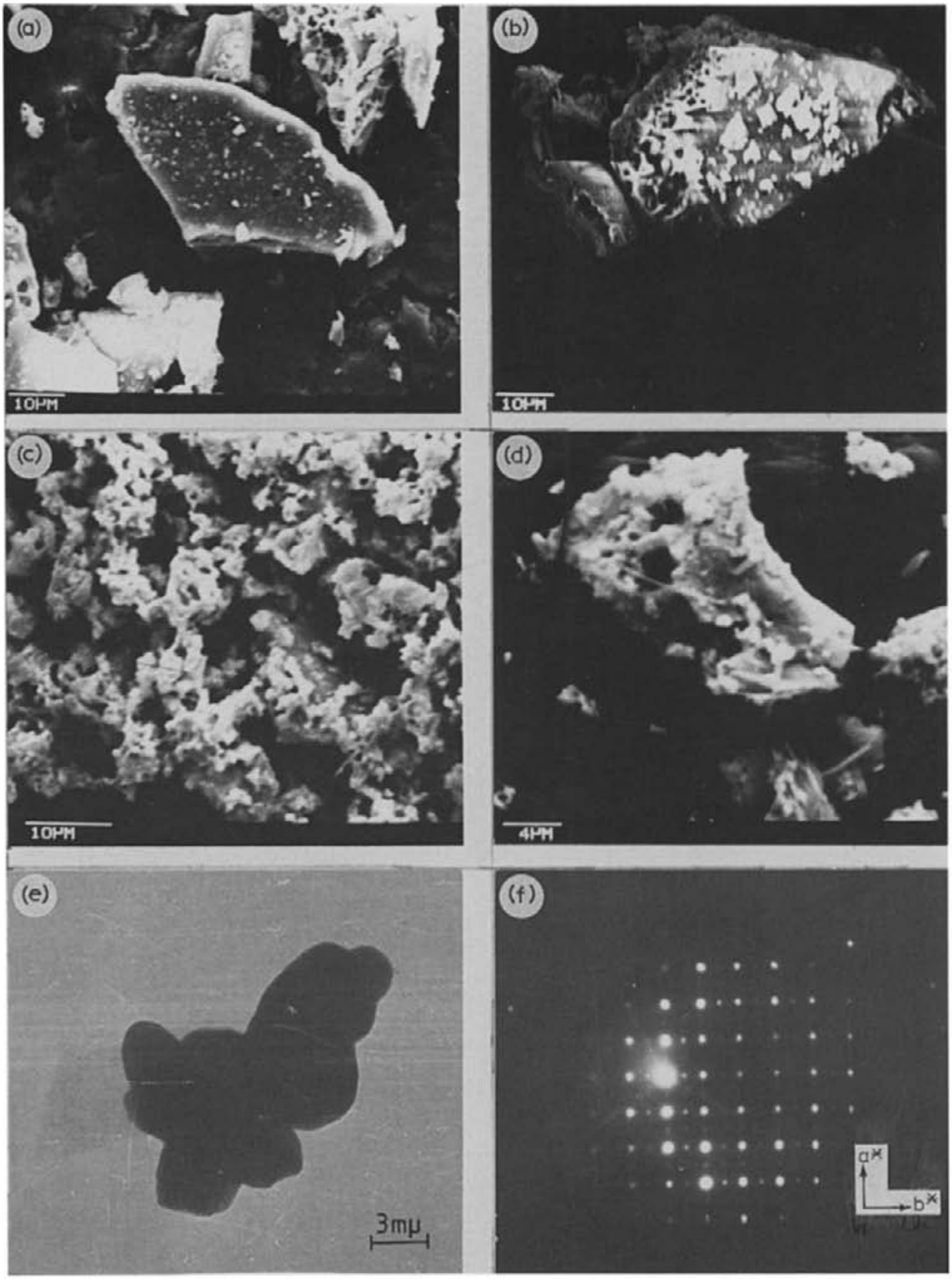

Fig. 2. Scanning electron micrographs of: (a) and (b) LCC; (c) and (d) $LaCrO_3$; (e) and (f) TEM and SAD of $LaCrO_3$.

be exothermic both in air and in argon, and considerable foaming was observed. Decomposition of the citrate started at around 475 K and was accompanied by evolution of CO_2 and H_2O. A weight loss of 50–52% was

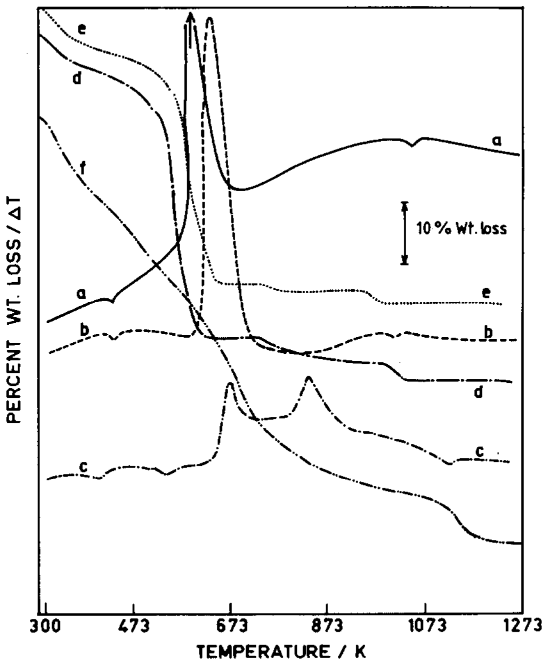

Fig. 3. TG and DTA curves for LCC: (a) and (d) in static air; (b) and (e) in flowing argon; (c) and (f) in mechanical mixture of lanthanum citrate and chromium citrate, in static air.

registered up to 625 K in air, as compared to the calculated value of 53.23% for the formation of the oxycarbonate, $LaCrO_2(CO_3)$. At the end of this step a stable oxycarbonate, $LaCrO_{3-x}(CO_3)_x$, was identified as the product. By isothermal heating of LCC in air at 640 K for 6 h, the isolated oxycarbonate was found to have a value of $x = 0.8$. Analysis of a sample of the residue gave La = 50.65%, Cr = 19.00% and CO_2 = 12.86%, which compared very well with the calculated values for $x = 0.8$ (La = 50.67%, Cr = 18.97% and CO_2 = 12.84%). The oxycarbonate was further identified by its IR spectrum, which showed absorptions at 1480, 1400, 920 and 820 cm^{-1}, similar to rare-earth oxycarbonates [19]. The value of x reached unity when preparation was in flowing oxygen, but only 0.4 in a flowing argon atmosphere. Furthermore, in argon the residue was black and contained nearly 8.5% carbon. The oxycarbonate was X-ray amorphous, though it showed partial crystallinity in electron diffraction.

Decomposition of the oxycarbonate

The oxycarbonate started decomposing above 700 K and the decomposition was almost complete at around 775 K in air. The observed weight loss of 4.3% was slightly more than the calculated value of 3.17%, but the total weight loss up to this stage of 57% compared favourably with the calculated 57.86%. The residue obtained by heating LCC at 725 K for 6 h in air was a

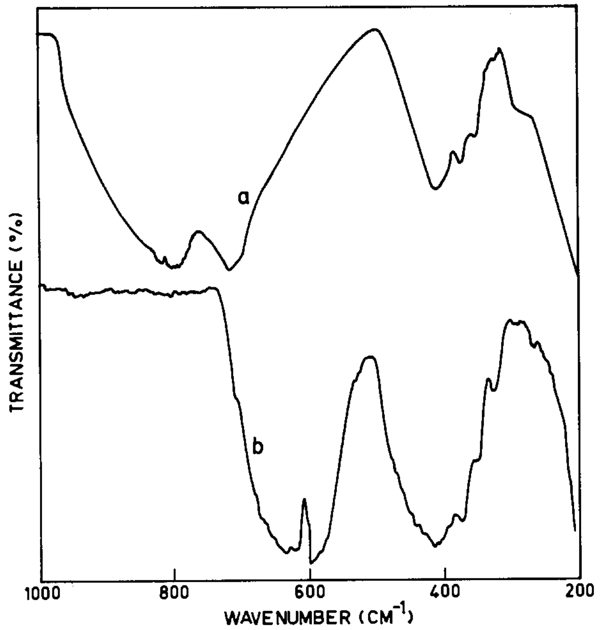

Fig. 4. IR spectra of: (a) $LaCrO_4$; (b) $LaCrO_3$.

dark green powder, which was analysed as having the composition $LaCrO_4$(V). The identity of the residue was further established by X-ray diffraction, IR electronic and ESR spectroscopy, and magnetic susceptibility measurements. The powder X-ray diffraction pattern can be fully indexed on the basis of a monoclinic lattice with $a = 7.05$ Å, $b = 7.25$ Å, $c = 6.71$ Å and $\beta = 104.8$ Å. This agrees very well with the reported lattice constants [20]. The IR spectrum (Fig. 4a) compares well with the spectrum expected for a tetrahedral oxyanion [21]. Aqueous extracts give an absorption band at 27100 cm^{-1} in the electronic spectrum, which can be assigned to the transition $t_1 \rightarrow 2e$ [22]. The solid in Nujol mull gives two strong bands at 31250 and 21612 cm^{-1}. These values are slightly lower than those obtained in the diffuse reflectance spectrum of $LaCrO_4$ [23]. Unlike the result reported previously by Roy and Nag [24], the present compound gives resonance signals in EPR at room temperature (300 K) as well as at 77 K. The g value of 1.88, though very low compared to a free electron, agrees with the previously reported [24] value.

The magnetic susceptibility of the compound was found to be 1.7 B.M., which is consistent with the d^1 configuration of Cr(V). In argon and other non-oxidizing atmospheres $LaCrO_4$ is not produced as an intermediate.

Decomposition of the orthochromate(V)

The final stage of decomposition was the loss of oxygen from $LaCrO_4$ to produce $LaCrO_3$. The observed and calculated weight losses correspond to the loss of 0.5 O_2 mol^{-1}. The residue obtained by isothermal heating of LCC in air at 875 K for 6 h was found to be $LaCrO_3$. The identity of the final residue was confirmed by X-ray diffraction. The lattice parameter calculated for a pseudo-cubic cell was $a = 3.888$ Å, which is in excellent agreement with earlier reports [25]. The actual symmetry of $LaCrO_3$ has been reported to be orthorhombic [26]. Electron diffraction studies on the powder revealed the true orthorhombic symmetry of the crystal (Fig. 2). $LaCrO_3$ prepared at 875 K had a surface area of ~ 7 m^2 gm^{-1} and the particles were compact, of average size 2.5 μm (Figs. 2c, 2d and 2e). Unlike the result reported by Nobuzo Terao [27], our sample of $LaCrO_3$ gave a monocrystal spot pattern (Fig. 2f) in electron diffraction. The IR spectrum of $LaCrO_3$ (Fig. 4b) consists of several medium and strong intensity bands, which are similar to those reported by Subba Rao and Rao [28] and Proskuryakova et al. [29]. The observed band maxima in the electronic spectra of the compound are as one would expect for Cr^{3+} in an octahedral crystal field. Two absorption bands appear in the electronic spectrum. The band at around 30 000 cm^{-1} is probably due to charge-transfer [30] and the band at around 16 360 cm^{-1} is due to the spin-allowed transition $^4A_{2g} \rightarrow {}^4T_{2g}$ [28]. The ESR spectrum of $LaCrO_3$ was recorded at various temperatures (Fig. 5) and resonance signals could be seen above 287 K. No signal was observed from 287 K down to 77 K. The change of ESR signal with temperature is probably due to magnetic transition in pure $LaCrO_3$, and the transition temperature of 287 K corresponds to the reported Neel temperature for $LaCrO_3$ [31]. The g value at room temperature was found to be 1.95.

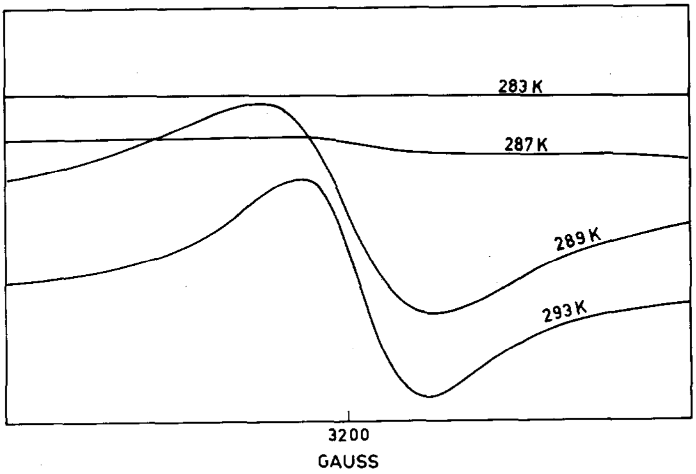

Fig. 5. ESR spectra of $LaCrO_3$ at different temperatures.

Thermal decomposition of a mechanical mixture of lanthanum citrate and chromium citrate

Thermal decomposition of mechanical mixture of lanthanum citrate ($LaC_6H_5O_7 \cdot 4H_2O$) and chromium citrate ($CrC_6H_5O_7 \cdot 9H_2O$) in molar ratio 1 : 1 was carried out in order to compare the behaviour of the mixture with that of LCC. A comparison of the thermograms (Fig. 2c and 2d) reveals that the mechanical mixture decomposes in a different way to LCC. The final residue at 1173 K is a mixture of La_2O_3 and Cr_2O_3, as identified by X-ray powder diffraction. This further establishes that LCC is a single phase containing both lanthanum and chromium in the complex.

DISCUSSION

Impure lanthanum chromium citrate complex has been reported [32] to decompose in three steps: removal of water of hydration and most of the nitrate; removal of the remaining nitrate and bonding of metal ions with carboxylate, producing a semi-decomposed mixed anhydrous citrate with some free carboxyl groups; and pyrolysis of anhydrous citrate to give $LaCrO_3$. Recently, the analogous lanthanum ferric citrate has also been shown [17] to decompose in three steps: the first step involves the elimination of free citric acid and nitrate, while the second and third steps correspond to break-up of the citrate complex and elimination of residual CO_3^{2-} and NO_3^-, respectively. In both cases, nitrate was present in considerable proportion.

In the present study neither free citric acid nor uncomplexed carboxylato groups were present, either in the starting complex or in any of the intermediates. In addition, NO_3^- was completely absent from the initial compound. The following scheme is therefore proposed for the decomposition for LCC in air.

$$LaCr(C_6H_5O_7)_2 \cdot 2H_2O \xrightarrow{360\text{–}400\ K} LaCr(C_6H_5O_7)_2 + 2H_2O \tag{1}$$

$$LaCr(C_6H_5O_7)_2 \xrightarrow{400\text{–}475\ K} LaCr(C_6H_3O_6)_2 + 2H_2O \tag{2}$$

$$LaCr(C_6H_3O_6)_2 + 9O_2 \xrightarrow{475\text{–}725\ K} LaCrO_{3-x}(CO_3)_x + 3H_2O + (12 - x)CO_2 \tag{3}$$

$$LaCrO_{3-x}(CO_3)_x + \tfrac{1}{2}O_2 \xrightarrow{725\text{–}990\ K} LaCrO_4 + xCO_2 \tag{4}$$

$$LaCrO_4 \xrightarrow{990\text{–}1100\ K} LaCrO_3 + \tfrac{1}{2}O_2 \tag{5}$$

The anhydrous complex can be isolated by isothermal dehydration of LCC at around 375 K. Steps (2) and (3) overlap, and represent the major reactions in the thermal decomposition of LCC. The actual reactions might be more complex than those represented by eqns. (2) and (3). Though no aconitate complex was isolated in the present study, it is presumed that the reaction proceeds through aconitate by analogy with the thermal decomposition of barium titanyl citrate hydrate [33]. Formation of $LaCrO_4$ requires either air or oxygen, and hence in non-oxygenic atmospheres like flowing argon (Fig. 2b and 2c) $LaCrO_4$ is not produced. The dehydration step and formation of the oxycarbonate are not affected by the surrounding atmosphere, except that x in $LaCrO_{3-x}(CO_3)_x$ tends towards unity in oxygen and towards around 0.4 in argon. In addition, considerable carbonization takes place in non-oxidizing atmospheres.

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