Journal of Analytical and Applied Pyrolysis 89 (2010) 250–254

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Thermal decomposition of lutetium propionate

J.-C. Grivel*

Materials Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, 4000 Roskilde, Denmark

ARTICLE INFO

Article history:
Received 21 May 2010
Accepted 30 August 2010
Available online 9 September 2010

Keywords:
Rare-earth propionate
Lutetium
Thermal decomposition
TG/DTA
IR
X-ray powder diffraction

ABSTRACT

The thermal decomposition of lutetium(III) propionate monohydrate ($Lu(C_2H_5CO_2)_3 \cdot H_2O$) in argon was studied by means of thermogravimetry, differential thermal analysis, IR-spectroscopy and X-ray diffraction. Dehydration takes place around 90 °C. It is followed by the decomposition of the anhydrous propionate to $Lu_2O_2CO_3$ with evolution of CO_2 and 3-pentanone ($C_2H_5COC_2H_5$) between 300 °C and 400 °C. The further decomposition of $Lu_2O_2CO_3$ to Lu_2O_3 is characterized by an intermediate constant mass plateau corresponding to a $Lu_2O_{2.5}(CO_3)_{0.5}$ overall composition and extending from approximately 550 °C to 720 °C. Full conversion to Lu_2O_3 is achieved at about 1000 °C. Whereas the temperatures and solid reaction products of the first two decomposition steps are similar to those previously reported for the thermal decomposition of lanthanum(III) propionate monohydrate, the final decomposition of the oxycarbonate to the rare-earth oxide proceeds in a different way, which is here reminiscent of the thermal decomposition path of $Lu(C_3H_5O_2) \cdot 2CO(NH_2)_2 \cdot 2H_2O$.

1. Introduction

Rare-earth propionates are being used more and more frequently in relation to the development of second generation high temperature superconducting (HTS) tapes; for the buffer layers [1–4] as well as for the superconducting layer itself [5–10]. Owing to the stringent microstructural requirements of this type of composite structures, like for example out-of-plane and in-plane preferential orientation within less than 10° and surface roughness of the order of 10 nm (rms) or better [11,12], it appears essential to control the conversion of the metal propionate based gel into complex oxides like $Gd_2Zr_2O_7$, $Ce(Gd)O_{2-\delta}$ or $REBa_2Cu_3O_7$ (RE = rare-earth) in the best possible way. Sparse studies dealing with the decomposition process of propionate based mixtures have been published [9] but the interpretation of the experimental data is rather difficult in view of overlapping decomposition steps taking place in the individual propionates and interferences between the decomposition products as well as other salts like e.g. Ba-trifluoroacetate. In order to better control the microstructural development of thin films manufactured by means of coatings containing metal propionates, it is necessary to start by studying the thermal decomposition behaviour of the individual components. A study of the conversion of Cu-propionate into CuO has been published by Kaddouri et al. [13]. In contrast, little is known about the thermal decomposition behaviour of rare-earth propionates. $La(C_3H_5O_2)_3 \cdot H_2O$ was reported to decompose to La_2O_3 via dehydration followed by the formation of a La-oxycarbonate ($La_2O_2CO_3$) [14], but, to the best of our knowledge, the thermal decomposition behaviour of other rare-earth propionates has not been reported yet.

The present work was undertaken in the framework of a research project aiming at understanding the details of phase and microstructure development in HTS coated-conductor tapes based on $REBa_2Cu_3O_7$. Although lutetium is not ordinarily used in conjunction with the manufacture of HTS tapes, it was interesting to study the thermal decomposition behaviour of its propionate salt as a starting point for systematic investigations, because Lu is the rare-earth element having the smallest radius compared to La, the only rare-earth propionate, which thermal decomposition has been reported in details so far [14].

2. Experimental

$Lu(CH_3COO)_3 \cdot 4H_2O$ from Alfa Aesar (99.9% purity (metal basis)) was dissolved in propionic acid (Alfa Aesar, 99%). After slow evaporation at room temperature without stirring, a white powder was obtained and used without further treatment for the thermal decomposition studies.

The thermogravimetry (TG) and differential thermal analysis (DTA) measurements were carried out up to 1400 °C in a model STA 449C from Netzsch (simultaneous TG/DTA device) at a heating rate of 5 K/min in a dynamic atmosphere consisting of argon at normal pressure. The gas flow was fixed at 40 ml/min. The crucibles (6 mm diameter and 3 mm depth) were made of alumina. Buoyancy corrections were performed using data recorded on empty crucibles. The sample mass was of 11.5 ± 0.2 mg for all measurements. The

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* Corresponding author. Tel.: +45 4677 4739; fax: +45 4677 5758.
E-mail address: jean@risoe.dtu.dk.

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doi:10.1016/j.jaap.2010.08.011

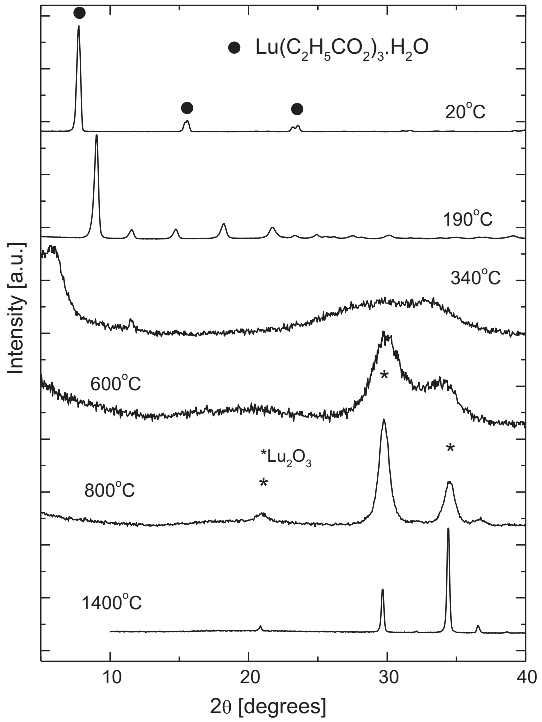

Fig. 1. XRD patterns recorded on the starting Lu $(C_2H_5CO_2)_3{\cdot}H_2O$ powder (20 °C) and on samples heated in the DTA/TG device at 5 K/min up to the indicated temperatures and fast cooled to room temperature.

powder was not compacted. α-Al_2O_3 powder (48 mg) was used as reference.

Fourier transform infra-red (FTIR) spectra were obtained with a Bruker Tensor 27 spectrometer coupled to the exhaust line of the TG/DTA device by a transfer line heated to 200 °C. FTIR spectra were also recorded on samples heated in the TG/DTA at a rate of 5 K/min and air quenched by opening the machine (up to 700 °C) or cooled at a rate of 50 K/min (from above 700 °C) in order to examine the evolution of the decomposition products. X-ray diffraction (XRD) patterns were collected on the same samples in a STOE diffractometer using CuK_α radiation.

3. Results and discussion

In the absence of published reference data for Lu-propionate, the synthesized product was characterized by comparison with other metal propionates. The XRD pattern of the as prepared sample is shown in Fig. 1 and is found to correspond well to the diffraction pattern published by Nadzharyan et al. [15] for $Y(C_2H_5CO_2)_3{\cdot}H_2O$. Furthermore, the FTIR spectrum (Fig. 2) contains the same features as those of $Ca(C_2H_5CO_2)_2{\cdot}xH_2O$ [16] and $La(C_2H_5CO_2)_3{\cdot}H_2O$ [14]. As will be shown in the following, the end decomposition product is Lu_2O_3 and the total relative weight loss (51.6 ± 0.1%) is in very good agreement with the loss expected for the conversion of $Lu(C_2H_5CO_2)_3{\cdot}H_2O$ to Lu_2O_3 (51.7%). Measurements under the same experimental conditions were performed on 5 powder samples with similar starting masses. The deviation in relative weight loss does not exceed ±0.2% and the temperatures, at which the different decomposition steps take place, are reproducible within 5 °C.

The TG trace recorded on an 11.41 mg Lu-propionate sample is plotted in Fig. 3 up to 1050 °C. The decomposition process is characterized by 4 weight loss steps. Steps b and c strongly overlap, but examination of the DTG trace (inset in Fig. 3) reveals a kink with inflection point around 395 °C. The DTA trace also plotted in

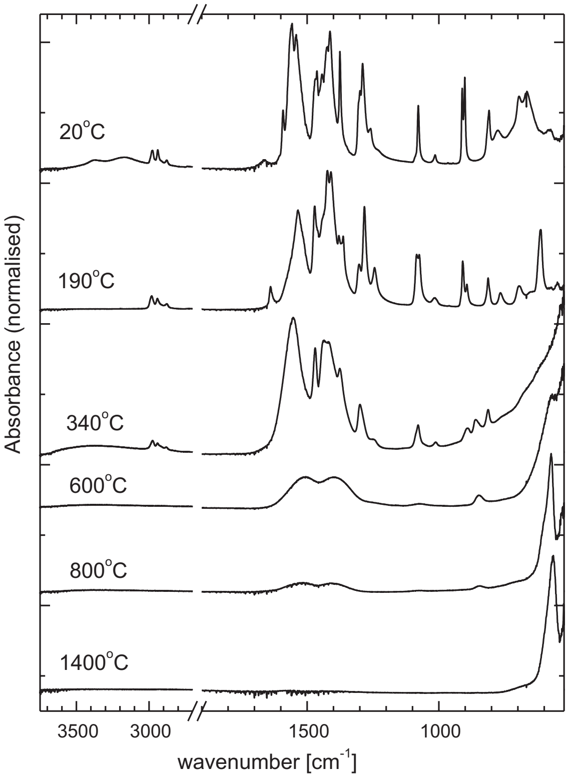

Fig. 2. FTIR spectra of the starting Lu $(C_2H_5CO_2)_3{\cdot}H_2O$ powder (20 °C) and on samples heated at 5 K/min in the DTA/TG device up to the indicated temperature and fast cooled to room temperature.

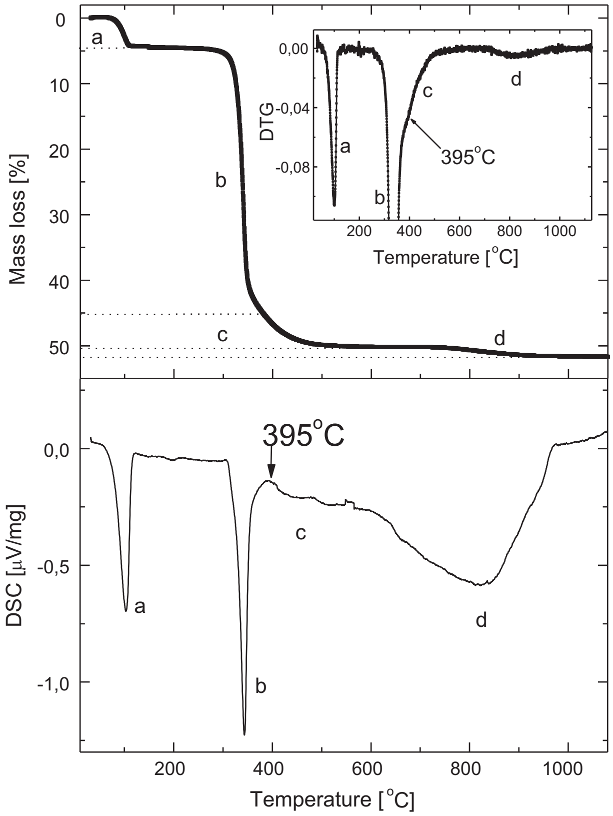

Fig. 3. Upper panel: TG trace recorded on Lu $(C_2H_5CO_2)_3{\cdot}H_2O$ at a heating rate of 5 K/min in flowing argon. Inset: Detail of the first derivative of the TG trace. Lower panel: DTA trace recorded on $Lu(C_2H_5CO_2)_3{\cdot}H_2O$ at a heating rate of 5 K/min in flowing argon.