



ELSEVIER

Contents lists available at ScienceDirect

## Materials Letters

journal homepage: [www.elsevier.com/locate/matlet](http://www.elsevier.com/locate/matlet)

# Low temperature crystallization of yttrium orthoferrite by organic acid-assisted sol–gel synthesis

Frédéric Stevens<sup>a</sup>, Rudi Cloots<sup>a</sup>, Dirk Poelman<sup>b</sup>, Bénédicte Vertruyen<sup>a</sup>, Catherine Henrist<sup>a,\*</sup>

<sup>a</sup> GREENMAT, Chemistry Institute B6, University of Liège (ULg), 3 Allée de la Chimie, Sart-Tilman, B-4000 Liège, Belgium

<sup>b</sup> Lumilab, Department of Solid State Sciences, UGent, Krijgslaan 281, S1, B-9000 Ghent, Belgium

## ARTICLE INFO

## Article history:

Received 3 July 2013

Accepted 27 September 2013

Available online 3 October 2013

## Keywords:

YFeO<sub>3</sub>

Sol–gel

Organic acid additive

Crystallization temperature

## ABSTRACT

Yttrium orthoferrite (YFeO<sub>3</sub>) is a promising material for visible light photocatalytic applications due to its band gap of 2.2–2.6 eV. However, during the synthesis of YFeO<sub>3</sub>, unwanted composition can be obtained and the crystallization requires temperatures as high as 850 °C. Powders of YFeO<sub>3</sub> were prepared using a sol–gel method with and without organic acids (citric acid, tartaric acid, malonic acid and oxalic acid) used as organic modifiers. The band gap of these powders was measured by diffuse reflection spectroscopy, and the crystallinity and crystalline phase content were characterized by X-ray diffraction. Organic acids allow a higher purity and facilitate crystallization. This work aims to produce YFeO<sub>3</sub> powders at the lowest possible temperature. Citric acid was found to be the best additive: it reduces the crystallization temperature below 450 °C. This opens new perspectives such as the deposition of crystalline YFeO<sub>3</sub> thin films onto conductive glass for water-splitting applications.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

A photocatalyst for water oxidation is made up of a semiconductor able to absorb sunlight. The most popular semiconductor for this application is TiO<sub>2</sub> in the anatase or a mixed anatase–rutile phase. Since the band gap of rutile and anatase is 3.05 eV and 3.2 eV respectively, ultraviolet light is needed to create electron–hole pairs and to activate the material for photocatalysis. The semiconductor band gap must be lower than 3 eV to allow activation by visible light. In addition, to initiate O<sub>2</sub> production, the conduction band (CB) level should be more negative than the dioxygen evolution level (EO<sub>2</sub>/H<sub>2</sub>O = 1.23 V vs NHE (pH = 0)) and the valence band (VB) level should be less negative than the dioxygen evolution level [1].

Various catalysts have already been used for water-splitting. Fe<sub>2</sub>O<sub>3</sub> is a semiconductor able to catalyze water oxidation under visible light and has been widely reported as such [2,3]. However it suffers from poor hole conduction and stability issues when in contact with corrosive aqueous solutions for long periods of time. Numerous other oxides are listed in specific reviews [1,4–6].

Yttrium orthoferrite is a semiconductor already registered as a photocatalyst for CO oxidation [7], and degradation of various compounds [8–11]. While the band structure of YFeO<sub>3</sub> is not well

described, its crystal structure being similar to that of Fe<sub>2</sub>O<sub>3</sub> and its band gap slightly broader than that of Fe<sub>2</sub>O<sub>3</sub> [12] make it an attractive candidate for water-splitting under visible light.

Many synthesis methods are reported: sol–gel [7,8,13,14], microwave-assisted [9,10], self-propagating combustion synthesis [11], solid state reaction [15], alkoxide method [16], sonochemical synthesis [17], pulsed laser deposition [18], etc. However, unwanted compounds can be obtained like yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) [11].

This paper reports the preparation of yttrium orthoferrite by simple sol–gel routes based on chloride or nitrate precursors, and the influence of organic additives on the purity and on the reduction of the crystallization temperature. Different groups mention the role of citric acid as a chelating agent to stabilize metal cations via the carboxylic acid group [1,7]. In this work, various organic acids were tested to obtain the purest YFeO<sub>3</sub>. Moreover, we noticed that the crystallization temperature is strongly reduced when organic acids are used.

## 2. Experimental section

The reactants were purchased from Sigma-Aldrich (FeCl<sub>3</sub> · 6H<sub>2</sub>O (99%), YCl<sub>3</sub> · 6H<sub>2</sub>O (99.9%), Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O (99%), L-tartaric acid (99%), citric acid (99.5%) and absolute ethanol), Alfa-Aesar (Y(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (99.9%)) and Acros Organics (HNO<sub>3</sub> 65% in water, NH<sub>4</sub>OH 25% in water, oxalic acid (99%) and malonic acid (99%)).

\* Corresponding author. Tel.: +32 43663438; fax: +32 43664747.

E-mail address: [catherine.henrist@ulg.ac.be](mailto:catherine.henrist@ulg.ac.be) (C. Henrist).

**Synthesis of  $YFeO_3$  powder based on chloride precursors (Cl route):** 50 ml of  $FeCl_3$  0.1 M in ethanol and 50 ml of  $YCl_3$  0.1 M in ethanol were prepared by dissolving  $FeCl_3 \cdot 6H_2O$  and  $YCl_3 \cdot 6H_2O$  in absolute ethanol respectively. These two solutions were mixed and stirred overnight before adding ammonium hydroxide (10%) to reach a pH of 7. The mixture was heated at 60 °C for 10 h to evaporate the liquid phase and obtain an orange paste. This paste is then transferred to a furnace with a heating ramp of 300 °C/h, up to 850 °C, and a stay of 2 h at this temperature. The resulting brown solid is then ground and analyzed by X-ray diffraction (XRD). This sample is named “Cl.”

**Synthesis of  $YFeO_3$  powder based on nitrates precursors (N(+ acid) route) [7,10,11]:** 20 ml of  $Fe(NO_3)_3$  0.1 M and 20 ml solution of  $Y(NO_3)_3$  0.1 M were prepared by dissolving  $Fe(NO_3)_3 \cdot 9H_2O$  and  $Y(NO_3)_3 \cdot 6H_2O$  in de-ionized water, respectively. These two solutions were mixed. We added solid organic acid (oxalic acid, malonic acid, tartaric acid or citric acid) to a concentration of 0.1 M and the final solution was stirred overnight. We added  $NH_4OH$  (10% in water) to reach a pH of 7. A clear sol was then obtained by adding a 2 M nitric acid solution. The sol was heated at 60 °C overnight to obtain an orange gel. If this gel contained organic acid, it was heated at 150 °C for 1 h on a sand bath because self-ignition occurs in some cases. Then, all the gels were heated at 450 °C or 850 °C. Every temperature was reached with a heating ramp of 300 °C/h and was kept for 2 h. The resulting fluffy brown solid was then ground prior to characterization. The samples were named N, N+oxalic, N+malonic, N+tartaric, and N+citric.

**Characterization of powders:** Purity and crystallization of the samples were characterized by powder X-ray diffraction (XRD) on a Siemens D5000 X-ray diffractometer with  $Cu K\alpha$  radiation.

The powder morphology was observed by Transmission electron microscopy (TEM) on a Tecnai G2 (FEI) with  $LaB_6$  filament and an accelerating voltage of 200 kV.

The percentage of crystalline phases was estimated by Rietveld refinement with the TOPAS software using the fundamental parameters approach to model the instrumental contribution [19]. The weight percentages of the different crystalline phases have been estimated by refining the scale factors and profile parameters using the cell parameters, atomic positions and occupation factors reported in references 04-010-6423 ( $YFeO_3$ ), 04-005-4378 ( $Y_2O_3$ ) and 04-003-2900 ( $Fe_2O_3$ ) of the PDF-4+ database (International Center for Diffraction Data).

The band gaps of the samples were obtained by converting, with the Kubelka–Munk function, the UV–vis–NIR diffuse reflectance spectra (DRS) obtained on a Varian Cary 500 using an integrating sphere.

### 3. Results and discussions

**Chloride or nitrate route:** The synthesis of  $YFeO_3$  at 850 °C based on chloride (Cl) or nitrate (N) precursors produces the desired yttrium orthoferrite phase ( $YFeO_3$ , PDF 00-008-0150) and, as side-products, yttrium oxide ( $Y_2O_3$ , PDF 00-001-0831), and iron oxide ( $Fe_2O_3$ , PDF 00-001-1053) for the Cl route (Fig. 1).

The nitrate route (N 850 °C) shows a smaller peak characteristic of  $Y_2O_3$  than that shown by the chloride route (Cl 850 °C). Furthermore, iron oxide is not detected in N samples. As a means of comparison between the different synthesis routes, the phase content of crystallized  $YFeO_3$ ,  $Y_2O_3$  and  $Fe_2O_3$  (Fig. 2) was determined via TOPAS software. This confirms that the N route gives rise to a lower contamination by  $Y_2O_3$  than that by the Cl route.

Precursors also influence the morphology of the powders. The nitrate-based sample (N 850 °C) seems, according to TEM images (Figs. 3 and 4), to be more porous than the chloride based one (Cl 850 °C). Indeed, during the nitrate route, self-ignition is observed.

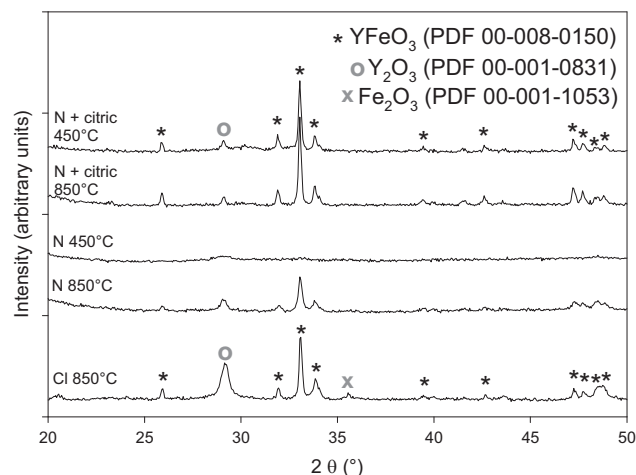


Fig. 1. XRD patterns of samples treated at 450 °C or 850 °C for 2 h.

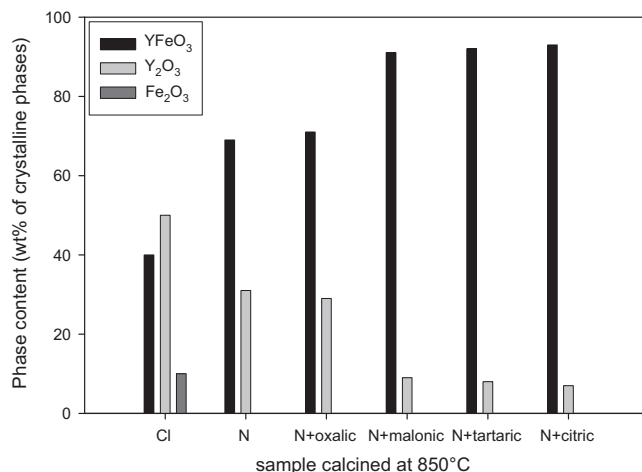


Fig. 2. Influence of precursor and/or organic acid on the phase content ( $YFeO_3$ ,  $Y_2O_3$  and  $Fe_2O_3$ ) for samples calcined at 850 °C/2 h.

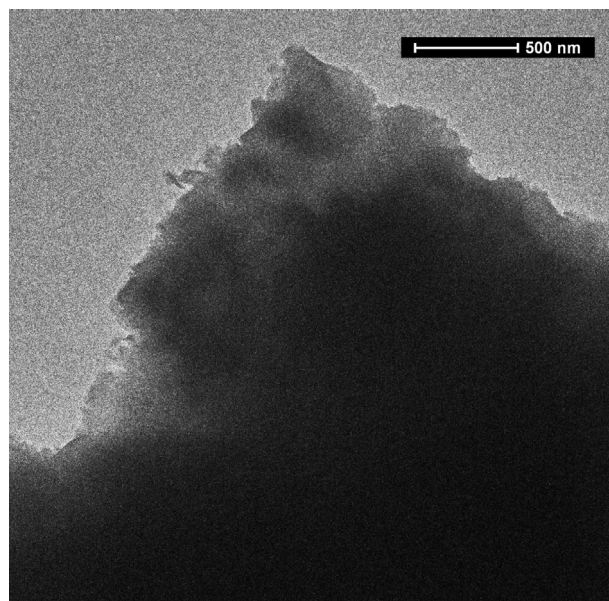


Fig. 3. TEM image of yttrium orthoferrite powder synthesized at 850 °C based on chloride precursor (Cl 850 °C).

Download English Version:

<https://daneshyari.com/en/article/1644865>

Download Persian Version:

<https://daneshyari.com/article/1644865>

[Daneshyari.com](https://daneshyari.com)