Journal of Physics and Chemistry of Solids 75 (2014) 265–270

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

Crystallization kinetics study of cerium titanate $CeTi_2O_6$

Václav Valeš [a,*], Lenka Matějová [b], Zdeněk Matěj [a], Tereza Brunátová [a], Václav Holý [a]

[a] *Charles University in Prague, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic*

[b] *Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Department of Catalysis and Reaction Engineering, Rozvojová 135, 165 02 Prague 6, Czech Republic*

ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form
1 October 2013
Accepted 11 October 2013
Available online 18 October 2013

Keywords:
A. Ceramics
B. Sol–gel growth
C. x-ray diffraction
D. Thermodynamic properties

ABSTRACT

Cerium titanate $CeTi_2O_6$ has been investigated recently for its photocatalytic activity and as a safe analogue to actinide-containing brannerite-like titanates (UTi_2O_6, $PuTi_2O_6$, e.g.) which are intensively studied because of their use for storing nuclear waste. In this paper we report on the monoclinic phase $CeTi_2O_6$ obtained from the Ti–Ce oxide mixture prepared by a reverse micelles directed sol–gel method and subsequently annealed. The kinetics of the isothermal crystallization process is investigated by means of Johnson–Mehl–Avrami–Kolmogorov equation. The effective activation energy of the formation of $CeTi_2O_6$ particles, which is an important parameter for its synthesis, is estimated.

1. Introduction

Titania–ceria mixed oxides have been studied recently because of their application potential in sensing films of gas sensors [1], as an electrode material in electrochromic devices [2], coatings for chemical–mechanical polishing [3], self-cleaning surfaces [4], photocatalysts with visible light induced activity [5,6] and catalysts support [7]. Various preparation methods based on sol–gel processes have been reported [1,2,4,5,7,8]. In a certain range of Ti:Ce content in the mixture, ternary cerium titanates [8–10] crystallize. These cerium titanates can form different phases with different oxidation states of Ce ions. In a reducing atmosphere during annealing process phases with Ce^{3+} ions are formed, such as Ce_2TiO_5, $Ce_2Ti_2O_7$, and $Ce_4Ti_9O_{24}$, while annealing in the air gives rise to Ce^{4+} ions containing phases, $CeTiO_4$, and $CeTi_2O_6$ [11]. Phases involving Ce^{4+} ions exhibit higher photocatalytic activity than those involving Ce^{3+} ions [11].

The structure of the monoclinic $CeTi_2O_6$ phase (space group $C2/m$, unique axis b) consists of zigzag layers of Ti atoms that are coordinated in distorted octahedra and layers of distorted Ce octahedra [12,13], see inset of the Fig. 4. The Ce atom is located in the Wyckoff position 2*a*, Ti and all oxygen atoms $O_{1,2,3}$ are in the positions 4*i*. A detailed structural study [14] has shown recently that the structure of $CeTi_2O_6$ is rather non-stoichiometric (should be expressed as $Ce_{1-x}Ti_2O_{6-2x}$, with $x=0.025$). However our study was not so sensitive to the presence of Ce and O vacancies, hence we assumed a stoichiometric form here ($x=0$). The crystal phase is isomorphous to the structure of UTi_2O_6 (brannerite), which is a part of synroc—a material developed to bind nuclear waste elements [12,15]. Since the study of actinide-containing materials is associated with difficulties, $CeTi_2O_6$ has been studied as their analogue—it has similar ionic radius and coordination environment [16,17].

In this paper we investigate the kinetics of crystallization of $CeTi_2O_6$ phase prepared by a reverse micelles directed sol–gel method. Earlier we studied four samples prepared by the same method with different ratios of Ti and Ce in the initial mixture (from 90% of Ti to 30% of Ti in molar units, see [18]), however in this paper we present the detailed results achieved for the mixture of nominal molar composition of 70% Ti and 30% Ce, since this particular sample after annealing consisted of almost pure monoclinic $CeTi_2O_6$. Understanding the crystallization process of cerium titanate is essential for optimizing the conditions of its preparation.

2. Experimental

2.1. Synthesis

We considered a series of four Ti–Ce oxide samples varying in the nominal molar ratio of Ti and Ce (Ti90–Ce10, Ti70–Ce30, Ti50–Ce50, and Ti30–Ce70) prepared in the free powder form and calcined for 4 h at 350 °C. Samples Ti90–Ce10 and Ti30–Ce70 crystallized into binary oxides of Ti (anatase and rutile) and Ce (cerianite) [18], sample Ti50–Ce50 contained crystalline cubic cerium oxide (cerianite), anatase TiO_2 and ternary phase of $CeTi_2O_6$. Sample Ti70–Ce30 crystallized to almost pure $CeTi_2O_6$ monoclinic phase with minor amount of anatase-TiO_2 (Fig. 1).

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[*] Corresponding author. Tel.: +420 221 911 482.
E-mail address: vales@mag.mff.cuni.cz (V. Valeš).

0022-3697/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jpcs.2013.10.001

In this paper we study in detail the kinetics of the formation of this ternary phase in the sample Ti70–Ce30 by means of x-ray diffraction.

For the synthesis of Ti70–Ce30 mixed oxide, the following chemicals were used: cyclohexane (Aldrich, HPLC grade), non-ionic surfactant Triton X-114 ((1,1,3,3-tetramethylbutyl)phenyl–polyethylene glycol, $C_{29}H_{52}O_{8.5}$, Aldrich), absolute ethanol (water content max. 0.2 vol%), titanium(IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, 99.999%, Aldrich), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6\,H_2O$, Aldrich) and distilled water.

Ti70–Ce30 mixed oxide as a powder was prepared via the sol–gel processing controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane and the thermal treatment [18]. The first step of synthesis consisted in the preparation of ceria sol: cerium(III) nitrate hexahydrate (1.1982 g) was dissolved in absolute ethanol (3 ml) under intense stirring. In the second step cyclohexane (16.4 ml) was mixed with Triton X-114 (14.4 ml) and distilled water (0.2 ml) followed by the addition of ceria sol. Prepared slightly yellow-coloured sol was stirred for 20 min. Titanium(IV) isopropoxide (1.887 ml) was injected fluently into the mixture in the final step. The micellar intensely yellow-coloured titania–ceria sol was stirred for other 20 min. After that the homogeneous transparent sol was poured into Petri's dish in a thin layer (~3 mm) and the dish was left standing on air up to the conversion of the sol into the gel. The gelation period was max. 60 h. Generally, the Ti70–Ce30 sol was prepared keeping the molar ratio of cyclohexane:Triton X-114:H_2O: $Ti(OCH(CH_3)_2)_4 + Ce(NO_3)_3 \cdot 6H_2O$ at 16.5:3:3:1 with the used amount of absolute ethanol 3 ml. The Ti70–Ce30 gel was scraped out from the Petri's dish to a calcination cup and thermally treated in air at 350 °C for 4 h with the heating rate 1 °C/min in order to produce 'as-prepared' Ti70–Ce30 brightly yellow-coloured powder for *in-situ* x-ray diffraction (XRD) studies. The calcination has been performed in order to convert the gel into the powder form. This conversion is accompanied by a removal of all organic part of the gel *i.e.* solvents, surfactant, organic rest of metal oxide precursors which were used in the preparation.

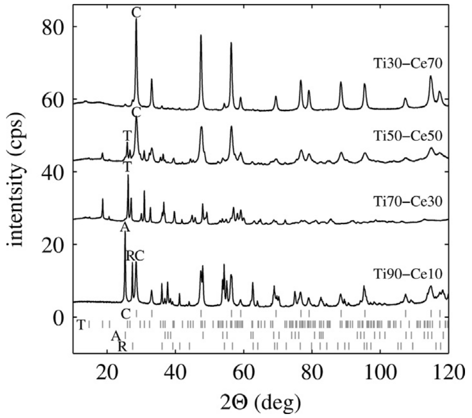

Fig. 1. Diffraction curves of samples with various content of Ti and Ce after annealing at 900 °C. The grey lines in the bottom correspond to diffraction positions of all phases found in the samples (C—cerianite CeO_2, T—ternary $CeTi_2O_6$, A—anatase TiO_2, R—rutile TiO_2). In the sample Ti30–Ce70 cerianite, rutile and anatase phases were found, in the sample Ti50–Ce50 cerianite, $CeTi_2O_6$ and anatase, in the sample Ti70–Ce30 $CeTi_2O_6$, and in the sample Ti90–Ce10 anatase, rutile, cerianite. The most intensive peaks corresponding to the major phases in the sample are indicated by the appropriate symbols.

2.2. *Characterization by non-diffraction methods*

We performed x-ray fluorescence (XRF), Raman spectroscopy, and nitrogen desorption experiments on the whole series of samples with different Ti:Ce content in our previous work. Details can be found in [18]. For the study here information on the actual molar composition of the samples is desirable. From the XRF analysis [18] for the sample studied in this work (nominally 70% of Ti atoms) the molar ratio of Ti atoms was found to be (72.2 ± 1.4)%.

2.3. *X-ray diffraction characterization*

X-ray diffraction curves were measured by the PANalytical-MPD diffractometer in the conventional focusing Bragg-Brentano geometry with variable slits using Ni-filtered CuK_α characteristic radiation. PIXcel linear detector was used for a fast collection of the scattered intensity in the diffraction angle range 10°–120°. The heating (up to 700 °C, in the air, heating rate 60 °C/min) was performed with a radiant heater placed around the sample. The sample was placed in an alumina crucible with a Pt–Rh thermocouple immersed into the sample inside the crucible. The annealing conditions were the same for all four temperatures, so

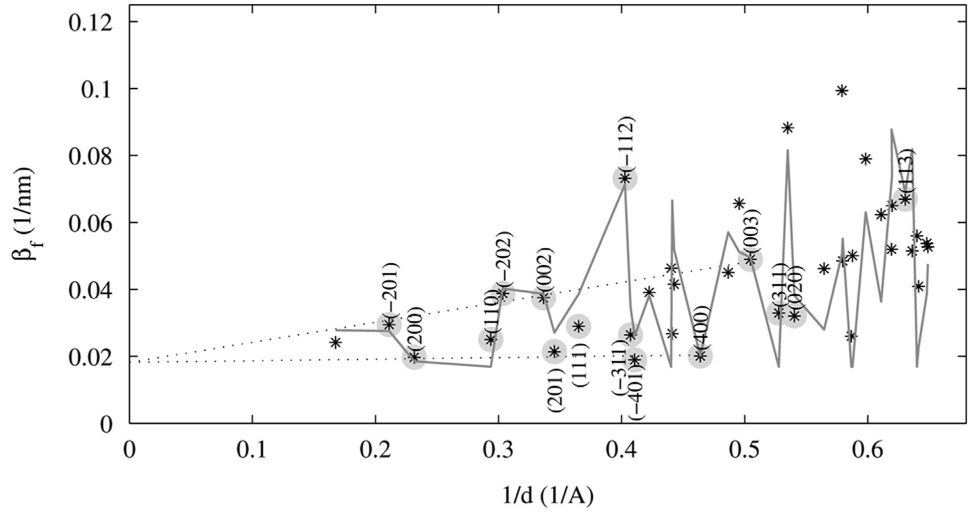

Fig. 2. The Williamson-Hall plot of selected diffraction peaks (black stars) of the *ex-situ* sample annealed at 650 °C. The anisotropy in strain can be seen in the data. For the fit of the anisotropy parameters, only clearly non-overlapping peaks were chosen (those with grey background). From the fit we calculated the integral breaths of the remaining diffractions (grey line). The dotted lines represent the linear fits of {*h00*} and {*00l*} diffractions with a common intercept at $1/d=0$. The plotted breadths were corrected for the instrumental broadening.