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Some peculiarities of zirconium tungstate synthesis by thermal decomposition of hydrothermal precursors

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ABSTRACT

This article discusses some peculiarities of the synthesis of ZrW_2O_8 (**1**) using thermal decomposition of the precursor $ZrW_2O_7((OH)_{1.5},Cl_{0.5})\cdot 2H_2O$ (**2**) prepared by hydrothermal method. On hydrothermal synthesis of **2** the optimal concentration of hydrochloric acid in the reaction mixture is about 2.3 M. TG approach to determine the chemical composition of the precursor was suggested. It has been found that the precursor for the synthesis of zirconium tungstate has chemical formula **2**. Thermal decomposition of the precursor **2** begins at 200 °C and affords an amorphous intermediate, which crystallizes as a cubic phase **1** above 550 °C with an exoeffect. The temperature of the beginning of the transition from amorphous to the crystalline state is 350 ± 25 °C.

1. Introduction

Zirconium tungstate **1** possesses a rare property of negative thermal expansion coefficient (TEC). It is known that at normal pressure zirconium tungstate can exist in three structural modifications [1–3]. Negative TEC is characteristic of cubic α- and β-ZrW_2O_8 as well as hexagonal **1** (h-ZrW_2O_8) [4]. Crystal structure of the cubic tungstate is formed by vertex-sharing octahedra ZrO_6 and tetrahedra WO_4. The phase transition from the low-temperature α-phase (space group $P2_13$) to the β-phase (space group $Pa\overline{3}$) occurs at the temperature of ~170 °C [1]. The phase transition consisted disordering of the WO_4 tetrahedra on the formation of the high-temperature phase. In recent years the nature and extent of local structural disordering in zirconium tungstate were studied rather thoroughly using neutron total scattering combined with reverse Monte Carlo modeling [5]. A trigonal modification of zirconium tungstate, isostructural to the trigonal zirconium molybdate $Zr_2Mo_2O_8$, was prepared using the sol–gel approach [3].

Traditionally, zirconium tungstate is prepared by solid phase interaction of zirconium and tungsten oxides at temperatures above 1100 °C [6–8]. However, this technique has an essential disadvantage: at high temperatures **1** undergoes incongruent melting accompanied by sublimation of tungsten (IV) oxide [9], often preventing synthesis of pure single-phase cubic zirconium tungstate. The synthesis is also complicated by partial decomposition of **1** on quenching as the compound becomes thermodynamically unstable below 1100 °C [10]. Therefore, preparation of zirconium tungstate at lower temperatures (below 700 °C), where it is kinetically stable, looks promising. Another way of obtaining **1** is a sol–gel method [11–14]. The powder prepared by the sol–gel method often contains decomposition products of matrix. One of possible approaches is hydrothermal synthesis, when **1** is prepared by decomposition of the precursor commonly described as $ZrW_2O_7(OH)_2(H_2O)_2$ at relatively low temperatures [15,16]. However, $ZrW_2O_7(OH)_2(H_2O)_2$ actually is a non-stoichiometric compound $ZrW_2O_7(OH_xCl_{2-x})\cdot 2H_2O$ [17]. An important factor affecting the hydrothermal synthesis of the precursor is the medium acidity – there are notices that higher acidity enhances yields [18,19], but

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quantitative data are missing. It is known that the synthesis of the material is accompanied both with chemical transformations and phase transitions, but detailed studies are unavailable.

The goal of this contribution is the synthesis and investigation of the precursor zirconium di(hydroxochloro) diaquatungstate, examination of the transformations occurring on the synthesis of **1** from this precursor.

2. Experimental

2.1. Materials and methods

The starting components for precursor preparation were aqueous solutions of $Na_2WO_4·2H_2O$ (0.5 M), $ZrOCl_2·8H_2O$ (0.25 M) and HCl (8 M). The solutions were prepared from $Na_2WO_4·2H_2O$ (“Krasnyii himik” St. Petersburg, Russia, p.a. (“Pure” >98%)), $ZrOCl_2·8H_2O$ (“Vecton” St. Petersburg, Russia, p. (“Chemically pure” >99%)) and HCl (“Reachem”, Russia, p. (“Ultrapure” >99%)). Aqueous solutions of $Na_2WO_4·2H_2O$ (25 mL, 0.5 M) and $ZrOCl_2·8H_2O$ (25 mL, 0.25 M) were thoroughly mixed, added with solution of hydrochloric acid of different concentrations (final concentrations were 0.4 M, 0.7 M, 1.4 M, 2.3 M), and stirred. The resulted suspension was placed into a Teflon-lined steel autoclave and kept at 160 °C for 12, 24 or 36 h for occurrence of the hydrothermal reaction. The product obtained was repeatedly washed with distilled water, collected on a filter and dried at the temperature of 110 °C. Yield ∼95%.

2.2. Instruments and measurements

High-temperature diffraction patterns were registered on a “Bruker D8” diffractometer using CuKα radiation. The diffractometer was equipped with a parabolic Goebel mirror (Bruker) affording pseudo-parallel X-ray beam and a graphite monochromator at the diffracted beam. A scintillation detector was used for registration. Scanning was carried out in 2θ range 10–70°, step size 0.02°, acquisition interval 3 s. High-temperature experiments were made with “Anton Paar HTK16 chamber” (Austria). All data were obtained in air at normal pressure. A sample was placed into the chamber, heated to the desired temperature and exposed to it for 15 min, and then the diffraction pattern was registered.

Phase composition was identified with powder diffraction database ICDD PDF-2 (2004) [20–22] and structural database ICSD.

Thermal analysis was made on “STA 449 F1 Jupiter” in a platinum crucible and oxygen–argon atmosphere (20% O_2).

Shapes and sizes of particles were examined with a scanning electron microscope “Philips SEM 515”.

3. Results

3.1. Synthesis of $ZrW_2O_7((OH)_5,Cl_{0.5})·2H_2O$

Powder diffraction patterns of samples obtained under different conditions of hydrothermal synthesis are shown in Fig. 1. The Miller indices of the XRD peaks attributed to **2** are shown in Fig. 2.

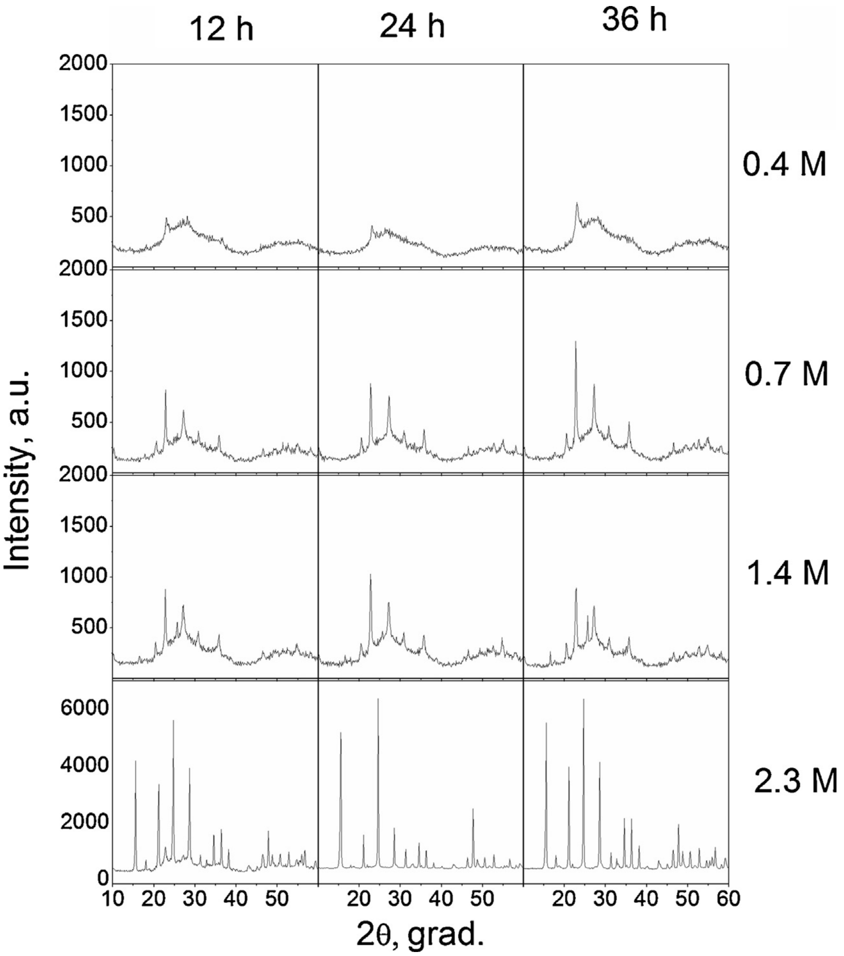

Fig. 1. Powder diffraction patterns of the samples obtained in different synthetic conditions (time, hydrochloric acid concentration). x axis – angle 2θ, y axis – intensity.