Hydrothermal Synthesis and Thermal Stability of Self-Assembling NH₄V₃O₇ Microcrystals

G. S. Zakharova, A. P. Tyutyunnik, Q. Zhu, Y. Liu, and W. Chen

Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences, ul. Pervomaiskaya 91, Yekaterinburg, 620990 Russia

Kirchhoff-Institut für Physik, Universität Heidelberg, Im Neuenheimer Feld 226, Heidelberg, DE-69120 Germany

Institute of Material Science and Engineering, Wuhan University of Technology, Luoshi Road 205, Wuhan, 430070 China

e-mail: volkov@ihim.uran.ru

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Abstract—Microcrystals of a new ammonium vanadate NH₄V₃O₇ phase self-assembling into 3D-spherical particles were synthesized via the hydrothermal treatment of NH₄VO₃ (T = 180°C, 48 h) in the presence of citric acid. The morphology of NH₄V₃O₇ particles was established to be governed by pH in the reaction mass. The compound crystallizes in monoclinic system with the unit cell parameters a = 12.247(5) Å, b = 3.4233(1) Å, c = 13.899(4) Å, β = 89.72(3)°, V = 582.3(4) Å³ (space group P2₁). The thermal stability and structural transitions of NH₄V₃O₇ during its thermolysis under air and an inert atmosphere were determined.

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Vanadium pentoxide and its derivatives attract the attention of a large community of researchers due to their unique structural flexibility and physicochemical properties and promise for use in catalytically active systems, chemical sensors, and elements of optical and electrical devices for microelectronics [1–3]. Recent works pay special attention to ammonium vanadates, which contain vanadium in a mixed oxidation state and provoke interest generally due to their promising application as the cathode material of reversible lithium current sources with a high discharge capacity combined with a low product cost [4–7]. Three low-dimensional ammonium vanadates with different ratios of four- and five-valent vanadium have been synthesized by now, namely, NH₄V⁴⁺V⁵⁺O₇·10H₂O, which can be written as (NH₄)₀.₅V₂O₅ [8–10], (NH₄)₂V⁴⁺V⁵⁺O₈ [11], and NH₄V²⁺V⁵⁺O₇ [12].

Different methods and approaches are used for the morphological control and synthesis of mixed ammonium vanadate nanostructures. Hydrothermal treatment is the most efficient, easily implementable, and low-cost method for the synthesis of nanosized compounds [13, 14]. For example, hydrothermal synthesis performed in the presence of sodium dodecylbenzene-sulfonate C₃H₇C₆H₄SO₃Na, an ionic detergent, yields ammonium vanadate (NH₄)₀.₅V₂O₅ with a morphology similar to nanobelts of 50–200 nm in diameter [6]. The diameter of (NH₄)₀.₅V₂O₅ nanobelts can be decreased to 30–40 nm by adding oxalic acid H₂C₂O₄·2H₂O (which acts as a mild reducing agent) to a reaction mass [7]. The use of a carboxymethylcellulose [C₆H₇O₂(OH)₃–x(OCH₂COOH)ₙ]ₙ template with x = 0.08–1.5 in the synthesis yields an ordered array of crossed (NH₄)₀.₅V₂O₅ nanobelts [15].

This study aims at elucidating conditions for the formation of NH₄V₃O₇ self-assembling microcrystals by a hydrothermal process, their morphology, and thermal and structural stability.

EXPERIMENTAL

Ammonium metavanadate NH₄VO₃ and citric acid C₆H₈O₇ (Sigma-Aldrich) were used as the initial compounds. Powder ammonium metavanadate was dissolved in water under stirring, therewith a saturated citric acid solution was added drop by drop to the resulting solution until a required value of pH was attained. The homogeneous solution was placed in an autoclave, allowed to stand at 180°C for 48 h, and cooled to room temperature. The thus-obtained black precipitate was filtered out, washed with water, and dried in air at 50°C. Powder morphology was studied on a Nano-SEM FEI scanning electron microscope with a built-in X-ray energy dispersion microanalyzer. X-ray diffraction analysis was performed on an XDDR-7000C Shimadzu diffractometer in air and a nitrogen flow using a high-temperature chamber. Thermal analysis was performed on a DTA 409 PC/PG Netzsch thermalanalyzer at a heating rate of 10 K/min from room temperature to 800°C in air and a nitrogen flow.

RESULTS AND DISCUSSION

According to X-ray diffraction data (Fig. 1, curve I), the hydrothermal treatment of ammonium metavana-
date at a working solution acidity of $4.0 \leq \text{pH} \leq 5.5$ adjusted with a saturated citric acid solution leads to the formation of a new $\text{NH}_4\text{V}_3\text{O}_7$ phase. $\text{NH}_4\text{V}_3\text{O}_7$ crystallizes in monoclinic system (space group $P_2_1$) with the unit cell parameters $a = 12.247(5)$ Å, $b = 3.4233(1)$ Å, $c = 13.899(4)$ Å, $\beta = 89.72(3)^\circ$, $V = 582.3(4)$ Å$^3$. The compound has a layered structure formed by vanadium oxide ($\text{V}_3\text{O}_8$)$^-$ layers oriented in parallel with the (101) plane. Ammonium ions are located in the interlayer spaces and form a network of hydrogen bonds with the terminal oxygen atoms of vanadium–oxygen polyhedra. When pH in the reaction mass is higher than 5.5 (Fig. 1, curve 2), the product contains $\text{NH}_4\text{V}_4\text{O}_{10}$ as an admixture phase (JCPDS 031-0075).

The morphology of the synthesized ammonium vanadate $\text{NH}_4\text{V}_3\text{O}_7$ was determined by scanning electron microscopy (SEM) (Fig. 2). According to SEM data, the sample synthesized at pH 4 consists of aggregated ball-shaped particles of 20–30 µm in diameter (Fig. 2a). Microspheres are built of chaotically crossed nanoplates of 50–200 nm in thickness and up to 2 µm in width (Fig. 2b). The morphology of the $\text{NH}_4\text{V}_3\text{O}_7$ sample changes as the reaction mass acidity decreases. Alongside with aggregated ball-like particles, there also exist individual nanoplates that build these microclusters. $\text{NH}_4\text{V}_3\text{O}_7$ particles consisting of square nanoplates organized into microassemblies of 15–20 µm in size (Fig. 2c) are formed when the reaction mass has pH 5.5. An individual plate has a thickness of 250–950 nm and a length of 5–15 µm. X-ray energy dispersion microanalysis (Fig. 3) confirms the purity of the synthesized product and the absence of foreign admixtures. An additional peak from carbon is produced by the substrate used to hold the sample.