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Preparation of tungsten-oxide, tungstate and molybdenum-oxide nanostructures by hydrothermal method

PhD thesis summary

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1. Introduction

The preparation of nanomaterials, the investigation of their new, unknown properties and their potential applications nowadays belong to the most important research fields. As the nanomaterials became conspicuous, the demand for such technological methods has increased, by which the most suitable structure, physicochemical characteristics etc. can be designed. In the case of chemical processes taking place on the surface of the materials (e.g. at photocatalysis, gas sensing) the optimal morphology and the size of specific surface area are particularly important, but for example the adsorption ability or the band gap energy can be also significant at different kinds of utilizations. From this point of view, the hydrothermal method offers a proper option, as the small differences in the reaction conditions can result significant changes in the properties of the products.

Due to its promising properties, tungsten-oxides (WO_3), tungstates (ZnWO_4 , CaWO_4 , Bi_2WO_6) and molybdenum-oxides (MoO_3) are intensively examined materials with potential applications. Possible fields of utilizations are (photo)catalysis, gas sensing, as well as the usage in electrochemical or solar cells [1-4]. Additionally, they are often prepared by hydrothermal processes.

During my PhD work I investigated the role of different reaction parameters (reaction temperature and time, pH of the precursor solution, additives) in the hydrothermal preparation of WO_3 , Bi_2WO_6 and MoO_3 , focusing on the formation of crystalline phases and morphology. One of the goals was to investigate such parameters which have not been studied at all or about which not enough data are available in the literature. On the other hand, other aim was to contribute, and extend the knowledge of the hydrothermal preparation of the mentioned compounds, thus provide further assistance to their synthesis with the desired phase and/ or morphology.

The hydrothermal synthesis of WO_3 was based on the reaction of sodium tungsten (Na_2WO_4) and hydrochloric acid (HCl). During the experiments I studied the effects of additives with different cations (Na_2SO_4 , FeSO_4 , $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, $\text{NH}_4\text{Fe}(\text{SO}_4)_2$, FeCl_3) and then additives with different anions (Na_2SO_4 , NaClO_4 , Na_3PO_4). Among them I was the first to study FeSO_4 , $\text{NH}_4\text{Fe}(\text{SO}_4)_2$, NaClO_4 and Na_3PO_4 . Then, the pH of the precursor solution was reduced from the generally used 1 to the value of 0.1. To clarify the effects of pH 0.1, reactions with and without various additives (CH_3COOH , Na_2SO_4 and NaClO_4) were carried out, which have not been reported in the literature yet. In order to understand the role of the reaction temperature, each synthesis was performed at 180 and 200 °C.

For the hydrothermal preparation of Bi_2WO_6 the reaction of Na_2WO_4 , HNO_3 and $\text{Bi}(\text{NO}_3)_3$ was used. Although, it is known that the pH of the precursor solution also plays a role in the formation of phases and in the process of crystal growth, mostly a part of it e.g., pH 1-7, 1-11, 4-8 etc. is investigated. So far only a few reports deal with the effect of the entire pH range. Therefore, after changing the reaction temperature (150/ 170/ 200 °C) and time (6/ 12/ 24 h) to determine the parameters that result the most crystalline Bi_2WO_6 phase, the pH of the reaction solution was also investigated. I was the first to study the entire pH range using 0.3/

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0.6/ 1.25/ 2.5/ 5.5/ 7.5/ 9.5/ 11.5 and 13.5 values, including the strongly acidic (pH <1) and also strongly alkaline (pH> 13) parts.

Finally, the reaction conditions in the hydrothermal synthesis of MoO₃ were examined. So far only α -(orthorhombic) and h-(hexagonal) phases of the different MoO₃ polymorphs have been prepared by this method, the metastable β - (monoclinic) MoO₃ not yet. As in the case of the preparation of MoO₃ the highest temperature is typically 200-210 °C, I chose also 240 °C besides 90 and 210 °C. The reactions were carried out not only at different temperatures (90/ 210/ 240 °C) and with different durations (3/ 6 h), but various additives - cetyltrimethylammonium bromide (CTAB) and chromium chloride (CrCl₃) – were also used. I was the first to study the effects of two reaction times, 3 and 6 h, and two additives, CTAB and CrCl₃ at such high temperature, at 240 °C.

2. Literature background

Hydrothermal method

The hydrothermal synthesis has become one of the most popular methods for preparing nanoscale materials in the recent decades, due to its simplicity and low energy demand. In the hydrothermal syntheses, the morphology and stoichiometry of the products can be easily controlled, and a large variety of nanopowders, composites and coatings can be produced with narrow particle size distribution, high purity and high degree of crystallinity. The hydrothermal process is a water-phase reaction taking place in a closed system (usually a pressure vessel, an autoclave) at a temperature higher than room temperature (usually at 100-250 °C) and a pressure higher than the atmospheric. Due to the high pressure generated, under normal circumstances insoluble reactants can be also used and metastable phases can be also prepared [5]. In many cases, there is no need for a post-heat treatment to increase crystallinity.

Hydrothermal preparation of tungsten-oxides

The preparation of WO₃ by hydrothermal process, using Na₂WO₄ and HCl starting materials, has been reported in many studies. An interesting feature of this reaction is that due to slight variations in the circumstances significant differences in the crystalline phases (orthorhombic, hexagonal, monoclinic) as well as in the morphology can occur.

It is known that depending on the quality of the additives, the morphology of the hexagonal (h-) WO₃ varies considerably. If (NH₄)₂SO₄ is added to the starting materials, nanofibers are formed, when Li₂SO₄ or Na₂SO₄ are used, nanorods are obtained. K₂SO₄ gives nanoribbon appearance, while Rb₂SO₄ results an urchin-like morphology, namely nanorods growing from the surface of microsphere. At the same time, not only the quality of the additives, but also the quantity has effect on the length and direction-dependent aggregation of the formed rods/ fibers [6,7].

The duration of the hydrothermal reaction is also an important parameter, as the length, diameter and uniform appearance of the h-WO₃ rods also vary depending on this [8,9].

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Increasing the amount of NaCl additive results transformation from 2D diamond-shaped forms to 3D nanoflower layout [10].

Increasing the pH value of the precursor solution, in addition to influencing the arrangement of the obtained rods, also affects the band gap energy of the products [11]. According to other reports, the different morphologies have role, for example, in the photocatalytic activity [12] or the gas sensing properties of the WO₃ products [13].

It can be seen that the additives used in the hydrothermal reaction of Na₂WO₄ and HCl have a decisive role in the obtained morphology of the product. However, effects of some additives have not been investigated yet or there is no available information about them in the literature. It is known, for example, that the presence of SO₄²⁻ anion leads to the formation of nanorod-like h-WO₃, when used along with NH₄⁺ or Na⁺ cations. On the other hand, if NH₄⁺ and Fe²⁺ are together present with sulphate, the product consists of FeWO₄ phase and even this is the case when FeCl₃ is used. However, the effect of single Fe²⁺ cation, and the NH₄⁺ together with Fe³⁺ ion, as well as the role of complex anions, e.g. ClO₄⁻ and PO₄³⁻, have not been studied yet.

Interestingly, mostly orthorhombic (o-) WO₃·H₂O and h-WO₃ are synthesized hydrothermally, while the preparation of monoclinic (m-) WO₃ by this method is generally carried out using a post- calcination step. However, the feasibility of a one-step, possibly additive-free synthesis would be useful, since m-WO₃ has much more advantageous properties than of other, WO₃ phases in photocatalysis or gas sensing [14].

Hydrothermal preparation of bismuth-tungstate

The most commonly used hydrothermal synthesis of Bi₂WO₆ is the reaction between Na₂WO₄, HNO₃ in the presence of Bi(NO₃)₃. Similarly to WO₃, Bi₂WO₆ can also be produced with a variety of morphologies, which can be achieved by the appropriate choice of temperature, reaction time, pH and additives.

The different pH values used in the syntheses not only affect the morphology of Bi₂WO₆, but the absorption and the band gap of the samples also depend very much on this, which all have a significant effect on photocatalytic efficiency [15,16]. It was found that in the case of Bi₂WO₆ prepared at different temperatures (100-240 °C) and durations (2-36 h), both the uniform nanoplate morphology and the degree of crystallinity, together with the size

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of the specific surface are highly dependent on both parameters, however more strongly on the reaction temperature [17].

Hydrothermal preparation of molybdenum-oxides

MoO₃ can be prepared with various crystal structures (hexagonal and orthorhombic) and different morphologies which is usually carried out with the usage of (NH₄)₆Mo₇O₂₄ (ammonium-heptamolybdate, AHM) and nitric acid (HNO₃). It is an interesting fact that the third phase, the metastable, monoclinic MoO₃, has not been synthesized by hydrothermal method yet.

Various additives are often used to influence the morphology of the resulting MoO₃. The CTAB additive with different concentrations (0-1 mM) benefits the transformation of the initial nanoribbon morphology into an urchin-like and plate-like forms [18]. The addition of CrCl₃ typically leads to a mesh-like morphology of the α -MoO₃ phase, while polyvinylpyrrolidone (PVP) favors the formation of irregular, variable-sized particles, both after a heating step of 500 °C [19,20].

Furthermore, the amount of PEG additive, acid concentration and reaction duration also play an important role in the formation of morphology. Increasing the concentration of acid, besides, affects the composition of the crystalline phase (hexagonal or orthorhombic), as well as photocatalytic activity [21,22]. Similarly, changes in the temperature of hydrothermal synthesis (140-200 °C) and duration (5-62 h) and also their combined effect play an important role in the appearance of the crystalline phase and morphology [23].

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3. Experimental methods

During my work, for the hydrothermal reactions I used a stainless steel pressure vessel, an autoclave equipped with a teflon liner. After preparing the reaction solution it was transferred into the autoclave which was placed in a furnace at certain temperatures and times. Finally, the products were filtered and dried.

The crystalline phase and the morphology of each sample were identified by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM), respectively. Some samples were further studied by other characterization methods: their elemental composition was investigated by energy-dispersive X-ray spectroscopy (EDX), their detailed morphology by transmission electron microscopy (TEM), and the specific surface area by nitrogen adsorption. In addition, I investigated their structural and light absorption properties by FT-IR, Raman and absorption (UV-Vis) spectroscopies, based on the latter I also determined the band gaps.

Hydrothermal production of tungsten-oxides

First, I studied the effect of various additives in the hydrothermal reaction of Na_2WO_4 and HCl, focusing on different cations and anions. Using the same anion (SO_4^{2-}) I tested Na^+ (Na_2SO_4), Fe^{2+} (FeSO_4), NH_4^+ and Fe^{2+} [$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ -Mohr salt], NH_4^+ and Fe^{3+} [$(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ - ammonium iron alum], and the addition of Fe^{3+} (FeCl_3). Then, using the same cation (Na^+), the following anions were used: SO_4^{2-} (Na_2SO_4), ClO_4^- (NaClO_4) and PO_4^{3-} (Na_3PO_4), alone or in combination with each other. After this, I reduced the pH of the precursor from pH 1 to 0.1. I studied the effect of this very acidic (pH 0.1) value without and with various additives (acetic acid (CH_3COOH in 1.25/ 2.5/ 5/ and 7.5 ml), NaClO_4 and Na_2SO_4). Due to the high similarity of the results in the case of acetic acid, only the results of the 1.25 ml CH_3COOH reaction are shown.

All reactions were performed at 180 °C and 200 °C to investigate the role of the temperature, with 24 h reaction duration.

Hydrothermal preparation of bismuth-tungstate

In the course of the hydrothermal synthesis of Bi_2WO_6 I aimed to determine the optimal reaction conditions for the most crystallized structure. Therefore I changed the reaction temperature (150/170/200 °C) and duration (6/ 12/ 24 h). Then, I used different precursor solution pH values (0.3/ 0.6/ 1.25/ 2.5/ 5.5/ 7.5/ 9.5/ 11.5/ 13.5) to investigate the influence of the entire pH range on the crystalline phases and morphology. When changing temperature and time, the pH value of the precursor solution was 0.3.

Hydrothermal preparation of molybdenum-oxides

In the hydrothermal reaction for the preparation of MoO_3 , increasing the temperature may lead to different phases, so I raised it from the initial 90 °C to 210 and 240 °C, and also the duration was changed from 3 h to 6 h. Moreover, various additives were tested: CTAB and CrCl_3 .

4. Results and discussion

Hydrothermal preparation of tungsten-oxides

In the case of additives with different cations, using Na_2SO_4 resulted pure h- WO_3 with nanorod morphology at both temperatures, with 50-300 nm thick at 180 °C and 150-200 nm width at 200 °C (Figure 1, A-B). Regarding FeSO_4 , a mixture phase containing h- WO_3 , Fe_2O_3 and FeWO_4 formed at 180 °C, the morphology of which was not uniform, i.e. sheets with nanoscale thickness (FeWO_4) along with smaller (50-100 nm, h- WO_3) and larger (1-2 μm) grains (Fe_2O_3) formed. However, at 200 °C, pure FeWO_4 was obtained in uniform 20-30 nm thick sheet-forms, which had not been previously reported in the literature (Figure 1, C-D). With all other additives, i.e. with $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and FeCl_3 , products with mixed phase and morphology were prepared at both temperatures.

When testing additives with different anions, I found that the usage of NaClO_4 additive gave pure o- $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ at 180 °C, and o- $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ with a small amount of m- WO_3 at 200 °C. In both cases, 50-200 nm thick, square shapes formed (Figure 1, E-F). When investigating the combined effect of Na_2SO_4 and NaClO_4 , pure phase h- WO_3 was produced at 180 and 200 °C, similarly to the products obtained when using only Na_2SO_4 (Fig. 1, G-H), but in this case the rods were more robust in size. In the case of Na_3PO_4 , no solid product was obtained during the experiments, with and without other additives (Na_2SO_4 or NaClO_4). The phenomenon may be explained by the formation of water-soluble phosphotungstates during the synthesis.

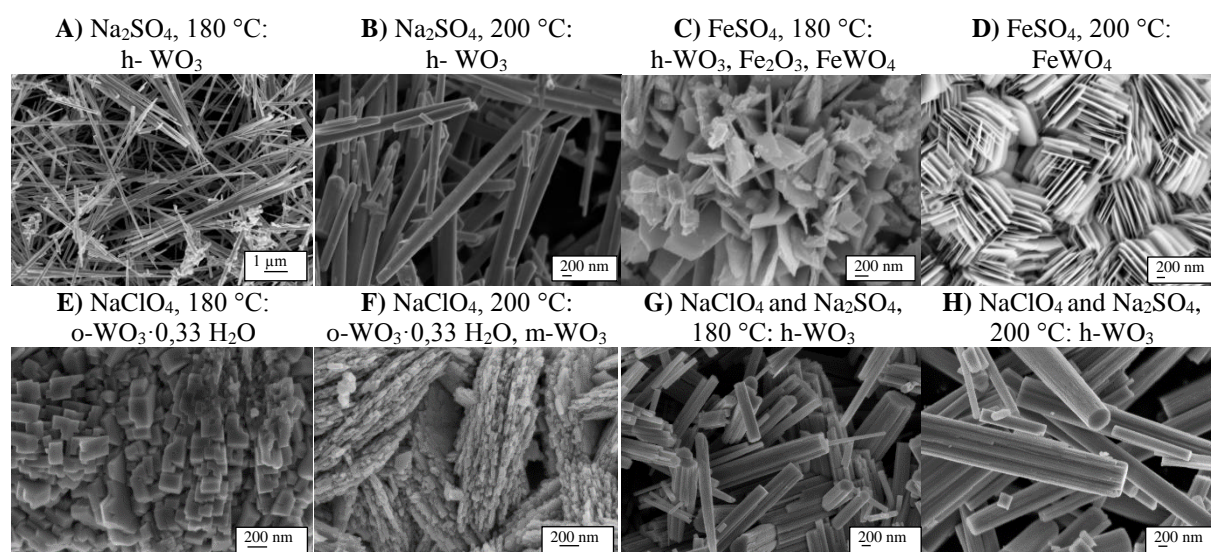


Figure 1: Products prepared in the hydrothermal reaction of Na_2WO_4 and HCl using various additives (180 and 200 °C, 24 h, pH 1)

In the hydrothermal reaction of Na_2WO_4 and HCl , the investigation was then continued by reducing the pH from 1 to the very acidic 0.1 value. First, hydrothermal reactions were carried out without additive and then with different additives (CH_3COOH , NaClO_4 , Na_2SO_4) at 180 and also at 200 °C. Based on the results, I found that independently of the presence and quality of the additives, m- WO_3 was obtained in all cases, with very similar, nanoplate morphology.

At 180 °C, the samples consisted of mainly sheets with 200-300 nm length, which were 20 to 200 nm thick when no additive was used. This average thickness for the CH_3COOH

additive was only 50-100 nm, while it was 50-150 nm for the NaClO₄ additive. However, the sample prepared with the usage of Na₂SO₄ had a greater size, thickness of 100-200 nm and a length of 350-800 nm (Figure 2, A-D).

At 200 °C, the nanosheets were, although, thinner than at 180 °C, only 20-100 nm thick when no additive, or when CH₃COOH or NaClO₄ additive was used, but became much longer, from 200 to 800 nm. However, in the case of the Na₂SO₄ additive, not only plates, but also 300-400 nm thick columns with a length of several μm formed. This can be presumably attributed to the well-known role of SO₄²⁻, in the anisotropic crystal growth, which also manifests itself under such a strongly acidic circumstance (Figure 2, E-H).

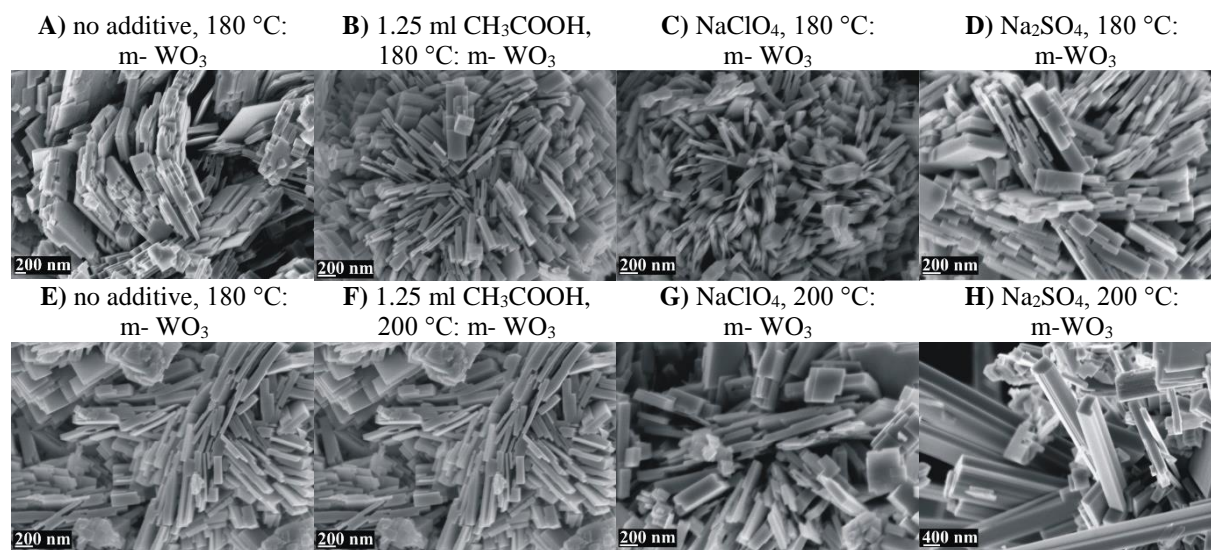


Figure 2: Products prepared in the hydrothermal reaction of Na₂WO₄ and HCl using pH 0.1 (180 and 200 °C, 24 h)

The obtained pure phase products such as h-WO₃ (Na₂SO₄, 180 °C, pH 1), FeWO₄ (FeSO₄, 200 °C, pH 1) and m-WO₃ (1.25 mL CH₃COOH, NaClO₄, Na₂SO₄, 180 °C, pH 0.1) were further studied. Their band gap and specific surface of the m-WO₃ samples were determined (Table 1). In the case of the pale yellow m-WO₃ samples the resulting electron structure was not affected by the quality of the used additive; thus, the band gap did not change significantly. According to the calculated band gap energies, the prepared materials are capable of absorbing visible light.

Table 1: Band gap and specific surface area of pure h-WO₃, FeWO₄ and m-WO₃ prepared in the hydrothermal reaction of Na₂WO₄ and HCl

	h-WO ₃	FeWO ₄	m-WO ₃ (1,25 ml CH ₃ COOH)	m-WO ₃ (NaClO ₄)	m-WO ₃ (Na ₂ SO ₄)
Bang gap energy(eV)	1.73	3.05	2.58	2.58	2.58
Specific surface (m ² /g)	-	-	9.0	11	5.8

Hydrothermal preparation of bismuth-tungstate

In the hydrothermal reaction of Na₂WO₄, HNO₃ and Bi(NO₃)₃ (at pH 0.3), all used temperatures (150/ 170/ 200 °C) and durations (6/ 12/ 24 h) resulted in pure Bi₂WO₆ phase. Based on the XRD patterns, I found that raising temperature and time improved crystallinity, which was indicated by the increasingly narrower and more intensive reflections. A uniform morphology of 10-20 nm thick and 200-400 nm wide sheets formed only when the reaction

parameters were 200 °C and 24 h. In all other cases a mixture of different forms could be observed.

In the case of samples prepared at different temperatures I also determined the band gap and the specific surface area (Table 2), which showed a clear temperature dependence. Higher temperatures favor an increase in the degree of crystallinity and the formation of larger crystallites.

Table 2: Band gap and specific surface area of pure of Bi_2WO_6 samples prepared at different temperatures (24 h, pH 0.3)

	Bi_2WO_6 (150 °C)	Bi_2WO_6 (170 °C)	Bi_2WO_6 (200 °C)
Band gap (eV)	2.66	2.68	2.59
Specific surface (m^2/g)	35.8	26	21.9

To investigate the effect of the entire pH range, I used the previously determined optimal conditions (200 °C, 24 h) and studied the morphology and crystalline phases by increasing the initial 0.3 pH value of precursor solution. In the acidic range (pH 0.3 to 5.5) every sample was identified as pure Bi_2WO_6 with variable morphology. The uniform appearance of sheets prepared at pH 0.3 gradually transformed into plate and fiber-like forms and other shapes with different sizes (Figure 3). At alkaline pH values (7.5-13.5), besides Bi_2WO_6 phase, $\text{Bi}_{3.84}\text{W}_{0.16}\text{O}_{6.24}$ also appeared, with reflections increasingly narrower and more intensive due to increasing pH, and finally it became the only phase at pH 13.5. This phase transition can also be followed in the SEM images, as well, as even at pH 7.5 the thicker, octahedral forms belonging to the $\text{Bi}_{3.84}\text{W}_{0.16}\text{O}_{6.24}$ phase are already visible. Upon further increasing the pH, they get more and more larger and ultimately it became the only component of morphology.

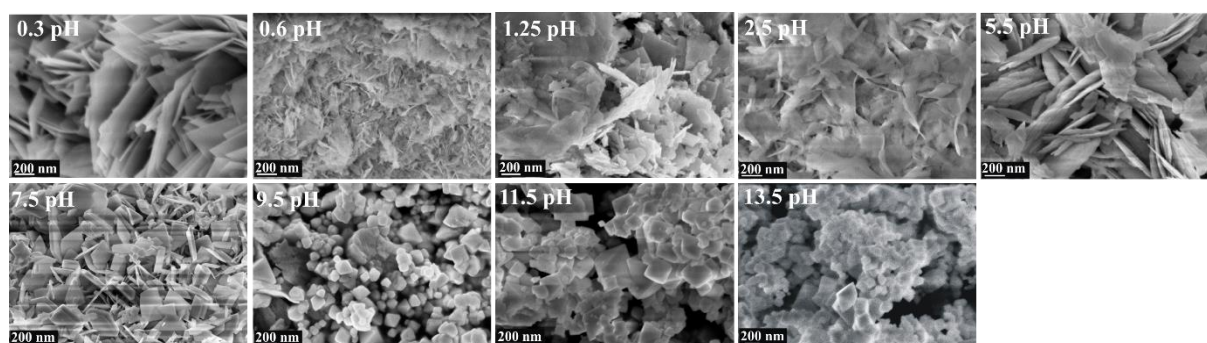


Figure 3: SEM images of the samples prepared at different pH values (200 °C, 24 h) (Bi_2WO_6 at pH 0.3-5.5 and $\text{Bi}_{3.84}\text{W}_{0.16}\text{O}_{6.24}$ at pH 7.5-13.5)

Hydrothermal preparation of molybdenum-oxides

For the preparation of MoO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and HNO_3 were used as the starting materials and the role of reaction temperature, time and the addition of CrCl_3 and CTAB additives were investigated in the formation of the crystalline phases and morphology.

First, the experiments were performed at 90 °C for 3 h and 6 h. In both cases, the product was pure, h- MoO_3 in the form of 10-50 μm long hexagonal rods (Figure 4, A). Raising the temperature to 210 °C resulted a product identified as a mixture of h- MoO_3 and α - MoO_3 at 3 h reaction duration but the synthesis for 6 h led to pure α - MoO_3 . The obtained morphology also reflected this transformation of the crystalline phases: in the 3 h reaction the hexagonal rods characteristic of h- MoO_3 formed together with nanofibers with a thickness of 100-200 nm and even several μm length. However, a uniform nanofibrous appearance was observed in the 6 h experiment (Figure 4, B-C). In the case of 240 °C, both the 3 h and also 6 h experiment resulted in pure α - MoO_3 with a morphology consisting of 200-400 nm fibers (Figure 4, D).

When using CTAB additive at 240 °C with both durations, α -MoO₃ was prepared, as well. Similar to the reactions carried out without additives at the same temperature, here also nanofibrous morphology formed, but in this case, the fibers were thinner, only 50-100 nm thick due to the effect of CTAB on the crystal growth (Figure 4, E). However, when CrCl₃ additive was tested, it resulted the formation of metastable β -MoO₃ in 3 h and also in 6 h synthesis time, at 240 °C. The hydrothermal preparation of this phase has not been reported in the literature yet. In contrast to the other phases prepared in the former experiments, the β -MoO₃ crystallized in the form of 50-200 nm thick, tightly ordered sheets.

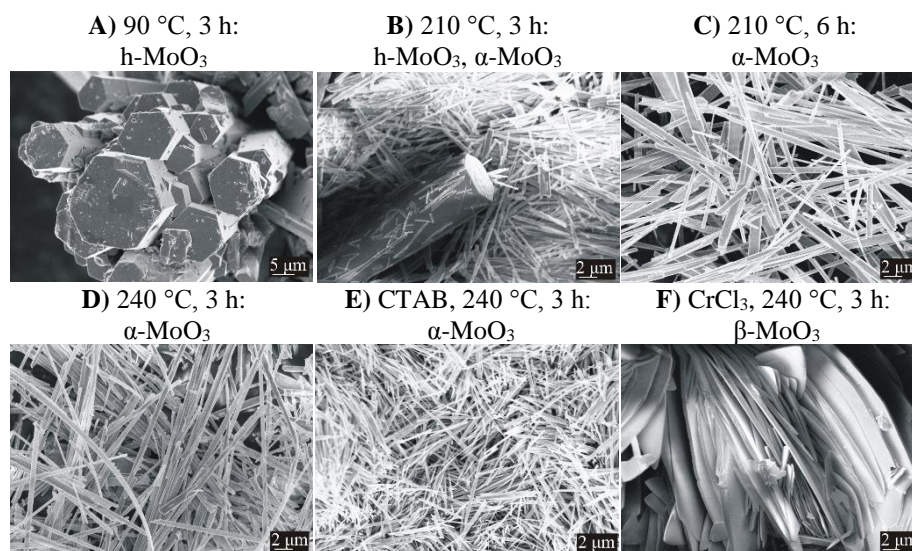


Figure 4: MoO₃ products with different phase and morphology prepared in the hydrothermal reaction of AHM and HNO₃

The band gap and the specific area of the different MoO₃ phases were determined (Table 3). The value of the band gap indicates that the samples can absorb also some visible light. The α -MoO₃ had the highest specific surface area due to its nanofibrous morphology, while the β -MoO₃ sheets and, especially the micro-sized h-MoO₃ columns had the much lower specific surface area.

Table 3: Band gap and specific surface area of the MoO₃ phases

	90 °C, 3 h: h-MoO ₃	CTAB, 240 °C, 3 h: α -MoO ₃	CrCl ₃ , 240 °C, 3 h: β -MoO ₃
Band gap (eV)	3.07	3.33	3.02
Specific surface (m ² /g)	0.21	9.6	2.4

5. Applications

The performed experiments have shown that the reaction conditions (temperature, time, precursor solution pH and additives) greatly influence the obtained crystalline phases and morphologies in the hydrothermal preparation of tungsten-oxides, bismuth-tungstate and molybdenum-oxides. By their careful choice, the certain phase and morphology can be reliably achieved, which can be easily influenced and modified by changing the reaction parameters.

The crystalline phase formed and the characteristic morphology determine the size of the specific surface and thus can be decisive in applications that use surface reactions. By increasing the surface, for example, the (photo)catalytic efficiency, gas detection properties, etc. can be improved. At the same time, also the crystal structure and the degree of crystallinity can contribute greatly to the usability.

Nevertheless, successful applications may require further optimization of features, for example, to reduce band gap energy, which can be achieved by formation of composites (e.g. with TiO₂, ZnO) or doping with noble metal nanoparticles (Pt or Au). However, increasing the specific surface area can also contribute to efficient use, which can be achieved by the adding of various additives, surfactants and precise selection of reaction parameters [24,25]. Based on these, study on the photocatalytic activity and efficiency of the new, hydrothermally previously not prepared phases ($m\text{-WO}_3$, $\beta\text{-MoO}_3$) would be useful in the future.

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6. Thesis statements

1. I found that in the hydrothermal reaction of Na_2WO_4 and HCl the FeSO_4 additive results in a mixed phase containing hexagonal WO_3 , Fe_2O_3 and FeWO_4 with nanosheet morphology at $180\text{ }^\circ\text{C}$, but only pure FeWO_4 forms at $200\text{ }^\circ\text{C}$. The usage of $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ additive, however, gives a mixed phase product at 180 and also at $200\text{ }^\circ\text{C}$. [1, 4]
2. I concluded that in the hydrothermal reaction of Na_2WO_4 and HCl the NaClO_4 additive leads to the formation of orthorhombic $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ phase in the form of rectangular nanostructures at 180 and $200\text{ }^\circ\text{C}$, similarly to the addition of Na_2SO_4 alone, demonstrating the decisive role of Na_2SO_4 in the crystal growth. Furthermore, I found, in the case of Na_3PO_4 additive solid phase product does not form due to the formation of water soluble phosphotungstates. [2]
3. I was the first prepare monoclinic WO_3 by a one-step hydrothermal reaction using no additive, and revealed the primary role of the strongly acidic pH of 0.1 in the formation of the monoclinic phase.
4. I found that using a strongly acidic ($\text{pH} < 1$) pH in the hydrothermal preparation of Bi_2WO_6 results in Bi_2WO_6 with nanosheet morphology, which transforms into octahedral $\text{Bi}_{3.84}\text{W}_{0.16}\text{O}_{6.24}$ phase due to the strongly alkaline pH range ($\text{pH} > 13$). [3]
5. I proved that the monoclinic MoO_3 can be prepared by a one-step reaction using CrCl_3 as additive.

7. Publications

Publications related to the dissertation

- [1] T. Nagyné-Kovács, Gy. Pokol, F.Gáber, D. Nagy, T. Igricz, I. E. Lukács, Zs. Fogarassy, K. Balázs, I. M. Szilágyi, Preparation of Iron Tungstate (FeWO_4) nanosheets by hydrothermal method, *Materials Research Bulletin* 95 (2017) 563–569, doi:10.1016/j.materresbull.2017.08.03 (IF 2017: 2.873, independent citations: 11)
- [2] T. Nagyné-Kovács, A. Malik, A. Szenkovits, I. E. Lukács, I. M. Szilágyi, Gy. Pokol, Effects of different anions upon the WO_3 morphology and structure, *Journal of Nanoscience and Nanotechnology* 19 (2019) 498-501, doi: 10.1166/jnn.2019.15790 (IF 2018: 1.354, independent citations: -)
- [3] T. Nagyné-Kovács, G. Shahnazarova, I. E. Lukács, A. Szabó, K. Hernádi, T. Igricz, K. László, I. M. Szilágyi, Gy. Pokol, Ph effect in the hydrothermal preparation of Bi_2WO_6 nanostructures, *Materials* 12 (2019) 1728, doi: 10.3390/ma12111728 (IF 2018: 2.972, independent citations: -)
- [4] S. I. Boyadjiev, T. Nagy-Kovács, I. E. Lukács, I. M. Szilágyi, Photocatalytic properties of h- WO_3 nanoparticles obtained by annealing and h- WO_3 nanorods prepared by hydrothermal method, *AIP Conf. Proc.* 1722 (2015), 140003-1–140003-4, doi: 10.1063/1.4944193 (IF: -, independent citations: -)

Publications partly related to the dissertation

- [5] T. Nagyné-Kovács, B. Mészáros, M. Molnár, M. Tolner, I. E. Lukács, I. M. Szilágyi, Gy. Pokol, Hydrothermal synthesis of Sr-doped hydroxyapatite and its antibacterial activity, *Periodica Polytechnica Chemical Engineering* (2019), doi: 10.3311/PPCh.14062 (IF 2018: 1.382, independent citations: -)
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- [8] C. M. Vladut, S. Mihaiu, I. M. Szilágyi, T. Nagyné Kovács, I. Atkinson, O. C. Mocioiu, S. Petrescu, M. Zaharescu, Thermal investigations of the Sn–Zn–O gels obtained by sol–gel method, *Journal of Thermal Analysis and Calorimetry* 136 (2018) 461–470, doi: 10.1007/s10973-018-7641-9 (IF 2018: 2.471, independent citations: -)
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- [10] I. M. Szilágyi, T. Nagyné Kovács, D. Hunyadi, A. L. A. De Lucena, Thermal decomposition of ammonium molybdates, *Journal of Thermal Analysis and Calorimetry* 124 (2016) 1013–1021, doi: 10.1007/s10973-015-5201-0 (IF 2016: 1.953, independent citations: 21)

8. Conference lectures and posters

Presentations related to the dissertation

1. Nagyné Kovács Teodóra, Nanoszerkezetű volfrám-oxidok és volframátok hidrotermális előállítására, Oláh György Doktori Iskola XVI. Konferencia, 2019, Budapest (lecture)
2. Teodóra Nagyné Kovács, Levente Studnicka, Gubakhanim Shahnazarova, Imre Miklós Szilágyi, István Lukács, György Pokol, Preparation of photocatalytic tungsten and molybdenum oxides and tungstates by hydrothermal method, Spring Meeting of the European Materials Research Society, 2018, Strasbourg, Franciaország (poster)
3. Nagyné Kovács Teodóra, Imre Miklós Szilágyi, István Lukács, György Pokol, Preparation of iron tungstate (FeWO_4) nanosheets by hydrothermal method, YUCOMAT, 2017, Herceg Novi, Montenegró (lecture)
4. Nagyné Kovács Teodóra, Imre Miklós Szilágyi, István Lukács, György Pokol, Preparation of iron tungstate (FeWO_4) nanosheets by hydrothermal method, Oláh György XIV. Oláh György Doktori Iskola PhD Konferencia, 2017, Budapest (poster)
5. Nagyné Kovács Teodóra, Imre Miklós Szilágyi, István Lukács, György Pokol, Preparation of iron tungstate (FeWO_4) nanosheets by hydrothermal method, International Conference of Physical Chemistry, Romphyschem 16, 2016, Galati, Románia (lecture)
6. Kovács Teodóra, Vas-volframát (FeWO_4) nanolemezek előállítása hidrotermális eljárással, XXXVIII. Kémiai Előadói Napok, 2015, Szeged (lecture)
7. Kovács Teodóra, Vas-volframát (FeWO_4) nanolemezek előállítása hidrotermális eljárással, XXXII. OTDK Konferencia, Kémiai és Vegyipari Szekció, Pannon Egyetem Mérnöki Kar, 2015, Veszprém (lecture)
8. Kovács Teodóra, Vas-volframát (FeWO_4) nanolemezek előállítása hidrotermális eljárással, BME-VBK TDK konferencia, Anyagtudomány és Polimerkémia Szekció, 2014, Budapest, second place (lecture)

Presentations partly related to the dissertation

1. Teodóra Nagyné-Kovács, Dávid Hunyadi, Alex Leandro Andrade De Lucena, Imre Miklós Szilágyi, Pokol György, Thermal decomposition of ammonium molybdates, ESTAC12, 2018, Brasov, Románia (poster)
2. Nagyné Kovács Teodóra, Studnicka Levente, Spengler Gabriella, Pokol György, Dr. Szilágyi Imre Miklós, Stronciummal és magnéziummal adalékolt hidroxipatitok előállítása és vizsgálata, MKE Analitikai Napok, 2018, Balatonszemes (lecture)
3. Teodóra Nagyné-Kovács, Dávid Hunyadi, Alex Leandro Andrade De Lucena, Imre Miklós Szilágyi, Thermal decomposition of ammonium molybdates, Oláh György XV. Oláh György Doktori Iskola PhD Konferencia, 2018, Budapest (poster)
4. Nagyné Kovács Teodóra, Studnicka Levente, Spengler Gabriella, Pokol György, Szilágyi Imre Miklós, Stronciummal és magnéziummal adalékolt hidroxipatitok előállítása és vizsgálata, PhD hallgatók anyagtudományi napja XVII., 2017, Pannon Egyetem, Veszprém (lecture)

5. Nagyné Kovács Teodóra, Studnicka Levente, Spengler Gabriella, Pokol György, Szilágyi Imre Miklós, Stronciummal és magnéziummal adalékolt hidroxipatitok előállítása és vizsgálata, XL. Kémiai Előadói Napok, 2017, Szeged (lecture)
6. Teodóra Nagyné-Kovács, Dávid Hunyadi, Alex Leandro Andrade de Lucena, Imre Miklós Szilágyi, György Pokol, Thermal decomposition of ammonium molybdates, 1st Journal of Thermal Analysis and Calorimetry Conference and 6th V4 (Joint Czech-Hungarian-Polish-Slovakian) Thermoanalytical Conference, 2017, Budapest (poster)
7. Kovács Teodóra, Ammónium-molibdátok termikus bomlása, MKE Termoanalitikai Szeminárium, 2015, Pécs (lecture)

