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Preparation of Nanocrystalline WO_3 and MoO_3 by Different Sol–Gel Methods

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Abstract

Two sol–gel methods for the preparation of WO_3 and MoO_3 nanopowders were used in this work: i) an ion-exchange reaction and ii) an oxidizing reaction ($M + H_2O_2$). The phase and structural transformations undergone by colloidal solutions of tungsten acid (i) and peroxotungsten and peroxomolybdic acids (ii) as a function of thermal treatment were investigated by X-ray diffraction (XRD) and infrared spectroscopy (IR). Depending on the methods used, different phases were obtained: crystalline hydrates, amorphous and nanocrystalline products. The tungsten trioxide hydrates were prepared by the ion exchange method, crystallization in m-WO_3 occurring above 300 °C. The tungsten sample being formed in the oxidizing reaction remained amorphous up to 300 °C; above 300 °C, m-WO_3 crystallized. The particle size of m-WO_3 was 15 nm irrespective of the methods applied. IR analysis showed that amorphous tungsten network was built by distorted WO_6 units without participation of peroxo groups (O_2^{-2}). The preparation of MoO_3 nanopowders by an oxidizing reaction was also studied. Crystallization of MoO_3 was found to start earlier (200 °C), leading to completely crystallized o-MoO_3 at 300 °C. The amorphous state of the product was detected at 100 °C only. Comparative analysis of the methods applied showed the oxidizing method to be more suitable for obtaining nanoparticles.

INTRODUCTION

WO_3 and MoO_3 are well known metal oxide materials used in gas sensing, catalytic, photochromic and electrochromic research fields. Depending on temperature, there are several crystalline modifications of WO_3 (triclinic, monoclinic, orthorhombic, tetragonal and hexagonal) [1, 2] while MoO_3 can exist in two polymorphous forms: orthorhombic and monoclinic [3]. All polymorphs of WO_3 can be described as distortions from the cubic ReO_3 structure, which consists of a three-dimensional network of corner-sharing WO_6 octahedra. The ReO_3 structure is characteristic of m-MoO_3 only. The monoclinic MoO_3 is transformed into orthorhombic MoO_3 at 400 °C. Crystalline o-MoO_3 has a layered structure of distorted MoO_6 polyhedra sharing both edges and corners. One oxygen in each polyhedron is unshared M=O [4]. From the practical point of view, the production of MoO_3 and WO_3 nanopowders is interesting. Several methods have been applied up to now: evaporation [5], sputtering [6] and sol–gel technology [7–14]. There are different sol–gel routes based on different starting compounds: polymerization and polycondensation of metal alkoxides [7], ion exchange methods [8–10] and oxidizing reaction of metallic W or Mo with a solution of H_2O_2 [11–13].

The purpose of this study is to obtain WO_3 and MoO_3 nanopowders using different sol–gel methods and to compare phase and structure transformations undergone by the precursors.

EXPERIMENTAL

Two different methods were selected in this study.

i) Ion exchange method (A). An aqueous solution of Na_2WO_4 was passed through ion-exchange resin to give the sol of tungsten acid [8]. The yellow sol obtained without any organic additives underwent gelation after 30 min at room temperature.

ii) Oxidizing reaction (B) between metal (W or Mo) powder and hydrogen peroxide solution ($M + H_2O_2$) [11]. The sol of peroxotungsten acid was obtained in the presence of ethanol and glacial acetic acid. The peroxotungsten acid was dried at 100 °C to remove the excess of hydrogen peroxide. The obtained sol underwent gelation after 48 h at room temperature.

MoO_3 was prepared by oxidizing reaction (B). The sol of peroxomolybdic acid was obtained without organic additives. The obtained sol was transformed into a gel at room temperature too slowly (after two weeks).

The samples obtained were investigated by X-ray phase analysis (APT-15 Philips diffractometer, CuK_α radiation) and infrared spectroscopy in the 1200–400 cm^{-1} region using the KBr pellet technique (Nicolet-320 FTIR spectrometer). The crystallite sizes were calculated using the Scherrer method for the (222) diffraction peak of monoclinic m-WO_3 and (111) diffraction peak of orthorhombic o-MoO_3 powders (the error of crystallite size determination is ±0.3 nm).

RESULTS AND DISCUSSION

X-ray diffraction analysis

X-ray diffraction patterns of the tungsten sample obtained by the ion exchange method and heated at 100–300 °C are shown in Fig. 1, a. There are principal peaks for $WO_3 \cdot 2H_2O$ ($d = 3.67$ Å, $d = 3.21$ Å, $d = 2.58$ Å), (18-1419 JCPDS) and for $WO_3 \cdot 0.33H_20$ ($d = 4.90$ Å, $d = 3.84$ Å, $d = 3.15$ Å), (35-0270 JCPDS). The ratio between the amorphous and crystalline phases is 1 : 1 (error 10 %). The thermal treatment above 300 °C leads to a visible improvement of the sample crystallinity which is indicated by a strong increase in the intensity of the peaks of m-WO_3 (83-0951 JCPDS) (see Fig. 1, b). The XRD pattern of the sample heated at 400 °C shows a trace of $WO_3 \cdot 2H_2O$. Similar results on the presence of hydrated tungsten oxide were obtained using Raman spectroscopy in [10]. The calculated crystallite size of the m-WO_3 powder is 14.5 nm at 400 °C and increases up to 16.7 nm at 600 °C.

The tungsten sample prepared by $W + H_2O_2$ reaction is amorphous up to 300 °C (Fig. 2). Above

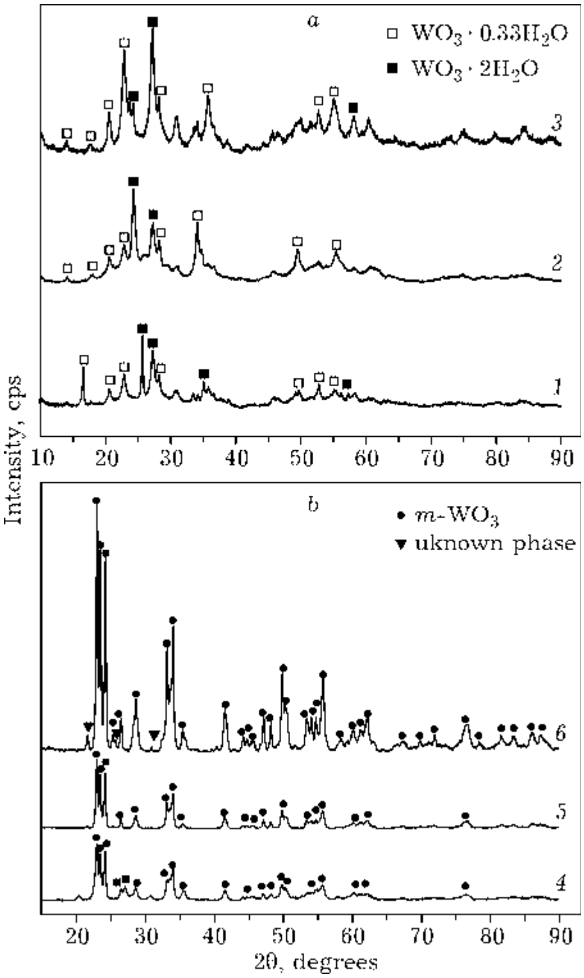

Fig. 1. XRD patterns of the tungsten sample obtained by method A. Temperature, °C: 100 (1), 200 (2), 300 (3), 400 (4), 500 (5), 600 (6).

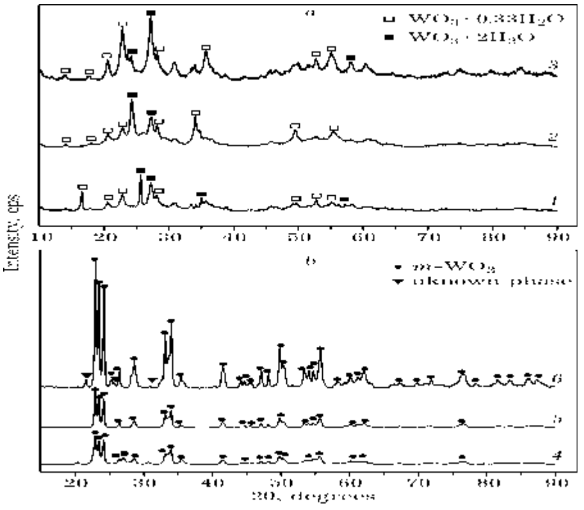

Fig. 2. XRD patterns of the tungsten sample prepared by method B. Temperature, °C: 100 (1), 200 (2), 300 (3), 400 (4).

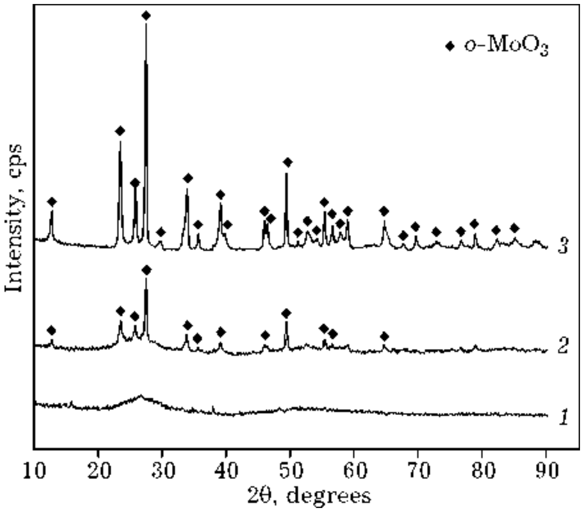

Fig. 3. XRD patterns of the molybdenum sample prepared by method B. Temperature, °C: 100 (*1*), 200 (*2*), 300 (*3*).

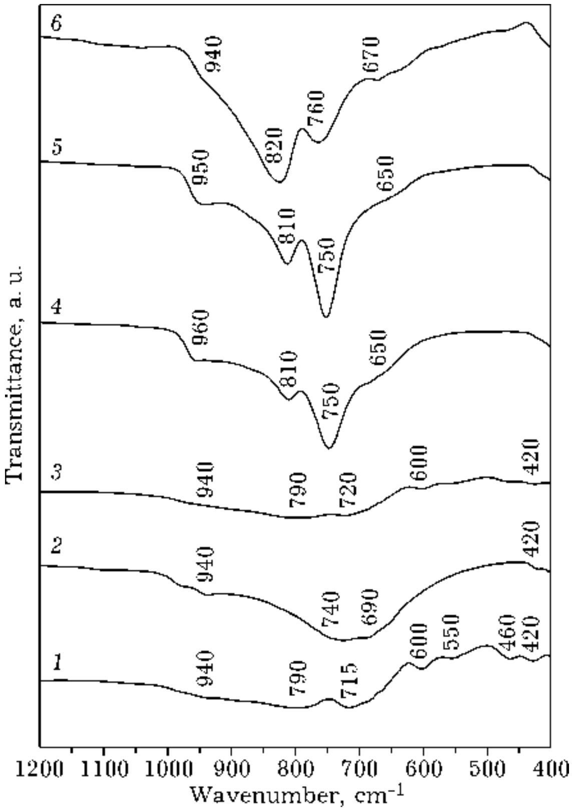

Fig. 4. IR spectra of the tungsten sample obtained by method A. Temperature, °C: 100 (*1*), 200 (*2*), 300 (*3*), 400 (*4*), 500 (*5*), 600 (*6*).

300 °C monoclinic WO_3 (83-0951 JCPDS) appears. The calculated crystallite size of *m*-WO_3 powder obtained by this method is 15 nm and does not change with further temperature rise.

The results of these studies show that the amorphous tungsten sample obtained by the oxidizing reaction is kinetically more stable.

Figure 3 presents the XRD patterns of the molybdenum sample obtained by Mo + H_2O_2 reaction and thermal treatment in the temperature range of 100–300 °C. In this case amorphous state is observed at 100 °C only. Further thermal treatment (200 °C) leads to partial crystallization of orthorhombic MoO_3 (35-0609 JCPDS) which completely crystallizes at 300 °C. The calculated crystallite size of *o*-MoO_3 powder is 25.8 nm.

Infrared analysis

Figure 4 shows the infrared spectra of the tungsten sample obtained by the ion exchange method. The bands characteristic of tungsten trioxide hydrates are observed in the spectra of the sample heated at 100–300 °C. The bands above 900 cm^{-1} are assigned to the stretching mode of the terminal W=O bond which is common for all types of $WO_3 \cdot nH_2O$ [2]. The bands between 800 and 600 cm^{-1} correspond to ν (W–O–W) stretching modes. The bands below 600 cm^{-1} are due to the bending modes of tungsten trioxide [8]. All bands characteristic of crystalline *m*-WO_3 are observed in the spectra of the sample treated above 300 °C. The presence of a high-frequency band at 960 (950) cm^{-1} in the spectra of the sample heated at 400 and 500 °C is an indication that the WO_6 polyhedra building *m*-WO_3 are distorted. The transformation of this band into a shoulder as well as the change in the intensity of the bands at 820 and 760 cm^{-1} in the spectra of the sample treated at 600 °C are probably a result of the formation of more symmetric WO_6 polyhedra.

The infrared spectra of the tungsten sample obtained by W + H_2O_2 reaction are shown in Fig. 5. The spectra of the sample treated at 100 and 200 °C contain bands characteristic of peroxo complexes: 980 cm^{-1} (νW=O), 900 cm^{-1} (νO–O), 810 cm^{-1} (νW–O–W) and 560 cm^{-1} (ν_{as}W–O–O) [14, 15]. The band at 650 cm^{-1} has a complex character and may be attributed to νW–O–W and ν_sW–O–O vibrations [15, 16]. It should be noted that at low pH of the solution mainly monoperoxo species are formed and a shift of the peroxo bands position to high wave numbers is observed [15]. The band at 560 cm^{-1} as-

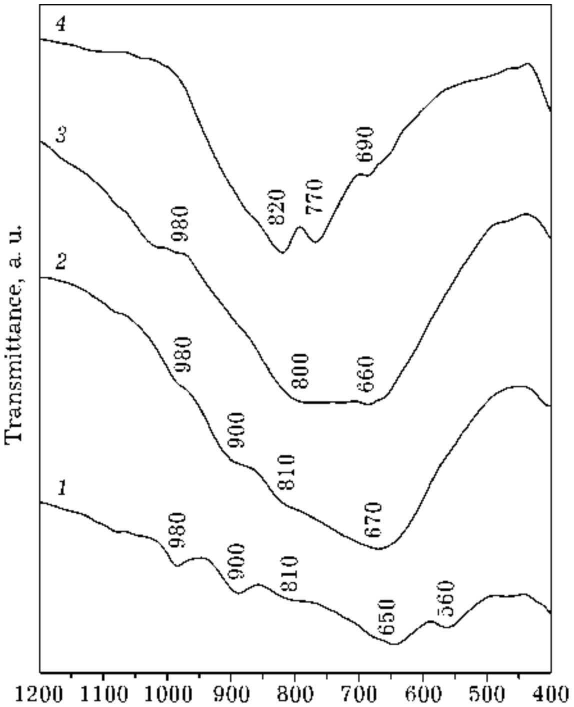

Fig. 5. IR spectra of the tungsten sample prepared by method B. Temperature, °C: 100 (*1*), 200 (*2*), 300 (*3*), 400 (*4*).

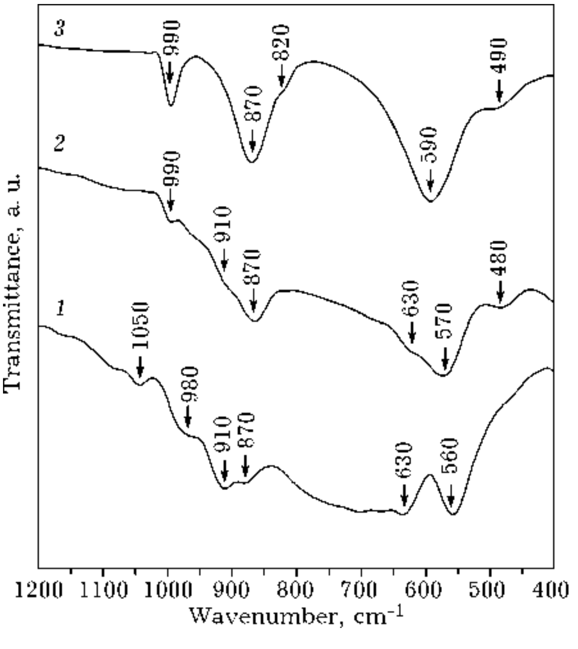

Fig. 6. IR spectra of the molybdenum sample obtained by method B. Temperature, °C: 100 (*1*), 200 (*2*), 300 (*3*).

signed to the vibration of peroxo (W–O–O) groups disappears at 200 °C while the band at 900 cm^{-1} attributed to the vibration of (O–O) bond vanishes at 300 °C. The weak band at 980 cm^{-1} and bands in the broad absorption region between 800 and 650 cm^{-1} in the spectrum at 300 °C can be assigned to stretching vibrations of distorted WO_6, building the amorphous network [11]. The presence of bands characteristics of WO_6 units is an indication that the number of peroxo groups (O_2^{-2}) decreases in the amorphous network formed at 300 °C . Bands typical of crystalline *m*-WO_3 appear in the spectrum of the sample thermally treated at 400 °C.

Figure 6 presents infrared spectra of the sample prepared by the Mo + H_2O_2 reaction. The spectra of the sample heated at 100 °C show bands characteristic of peroxo complexes: 980 cm^{-1} (νMo=O), 910 cm^{-1}(νO–O), 870 cm^{-1}(νMo–O–Mo), 630 cm^{-1}(ν_sMo–O–O) and 560 cm^{-1} (ν_{as}Mo–O–O) [14, 15]. The bands at 910 and 630 cm^{-1} characteristic of peroxo groups are transformed into shoulders with increasing temperature (200 °C) and disappear at 300 °C. The infrared spectrum of the sample thermally treated at 300 °C is typical of *o*-MoO_3.

CONCLUSIONS

1. Depending on the method and thermal treatment used, it is possible to obtain different tungsten phases: crystal-like hydrates, amorphous or nanocrystalline *m*-WO_3.

2. The final product at 400 °C is the same (*m*-WO_3) irrespective of the methods applied. The average crystallite size is 15 nm.

3. With peroxo sol–gel methods, nanocrystalline MoO_3 powder is obtained. The average crystallite size is 25 nm.

4. In comparison with WO_3, crystallization of MoO_3 starts at a lower temperature (200 °C).

5. It is established that the use of the method B is more appropriate for the preparation of nanocrystalline WO_3 and MoO_3.

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