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Microwave Synthesis of Cadmium and Zinc Tungstates

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The possibility of zinc and cadmium tungstate synthesis by reaction of metal nitrates with ammonium paratungstate by microwave irradiation is studied. Formation of the metal tungstate begins in a liquid phase at the melting point of initial hydrates and is completed at their complete decomposition temperature, at 400-450°C. The microwave activation does not have influence on the mechanism of cadmium and zinc tungstate synthesis, but it considerably accelerates it. It is shown that, during the microwave activation, cadmium tungstate, with scheelite structure (a = 5.170 Å, c = 11.140 Å), is formed.

Keywords metal tungstate, microwave synthesis

1. Introduction

The microwave (MW) radiation is used as rapid method of heating of the different dielectric materials and their mixtures in the different aggregate states (Ref 1-3). One of successful applications of MW energy is the activation of chemical reactions for synthesizing organic and inorganic compounds (Ref 2-6). It is noted in the literature that the MW irradiation allows a considerable acceleration of the reactions and a decrease in interaction time, in comparison with traditional thermal heating. The reaction mixture is heated in bulk which avoids temperature gradients within the reactor and excludes local overheating effects. The vessel walls are not heated since MW energy is transferred directly into the reactants.

In spite of the fact that basic attention of researchers during the MW activating of the chemical processes is concentrated in the area of organic synthesis, a sufficient number of papers for MW inorganic synthesis have appeared. Among those papers, a significant amount relates to the synthesis of the different oxides materials (tungstates, vanadates, titanates, and other) with various particle sizes and morphologies (Ref 6).

Among all claimed functional materials, the tungstate bivalent metals are specially distinguished and are currently used in many areas of science and technology (Ref 7-9). In particular $CdWO_4$ and $ZnWO_4$ are being used in nuclear spectrometry (Ref 10), dissymmetric, and computer tomography (Ref 11-14). Cadmium and zinc tungstates are obtained by different methods: heating of tungsten oxides with metal oxides or carbonates (Ref 15-17), synthesis in water solution (Ref 18), sol-gel (Ref 19), and hydrothermal synthesis (Ref 20).

In spite of the variety of the offered methods, the basic method of tungstate synthesis is thermal interaction between metal and oxides; it is characterized by synthesis temperatures of more than 800 °C and reaction times of about several hours. Replacement of metal oxide by metal nitrate or carbonate, and WO_3 by ammonium paratungstate can be instrumental for decreasing the metal tungstate synthesis temperature. For reaction intensification, it is possible to use the MW radiation.

In this work the MW activation of zinc and cadmium tungstates formation, by decomposition of mixture of cadmium or zinc nitrates and ammonium paratungstate, is described.

2. Experimental

2.1 Materials Preparation

$Cd(NO_3)_2{\cdot}4H_2O$ (99.9%), $Zn(NO_3)_2{\cdot}6H_2O$ (99.9%), and ammonium paratungstate (99.9%) were purchased in "Reachim". All chemicals were used without additional purification. The solutions were prepared using distilled water as solvent.

2.2 Synthesis Process

2.2.1 MW Preparation of Cadmium Tungstates. 12.85 g of $Cd(NO_3)_2{\cdot}4H_2O$ and 10.8 g of ammonium paratungstate were ground for 10 min to form a homogeneous mixture and pushed in a quartz ampoule which was installed in the waveguide of a MW synthesis stand. MW energy varied from 100 to 1000 W, reaction time was between 5 and 20 min and the frequency 2.45 GHz was used. After the irradiation a sample was collected from the quartz ampoule.

2.2.2 MW Preparation of Zinc Tungstates. 14.25 g of $Zn(NO_3)_2{\cdot}6H_2O$ and 12.42 g of ammonium paratungstate were ground for 10 min to form a homogeneous mixture and pushed in a quartz ampoule which was installed in the waveguide of a MW synthesis stand. The heat treatment mode was the same as with the synthesis of cadmium tungstate.

2.2.3 Thermal Synthesis of Metal Tungstates. The quartz ampoule with 30 g of metal nitrate and ammonium paratungstate mixture taken in equivalent amounts was installed in preliminary heated to the temperature 500 °C stove. The synthesis time was 40 min. Then the quartz ampoule was cooled to the room temperature the powder was collected.

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2.3 Characterization

FT-IR spectra have been taken by using a SPECTRUM ONE (PerkinElmer) infrared spectrometer with spectral resolution of 1 cm^{-1}. The X-ray diffraction (XRD) patterns of the sample was measured on a Siemens D500 diffractometer with use of monochromatized Cu K_α radiation (λ = 1.5418 Å) at 40 kV and 100 mA. The scanning range was $10° < 2\theta < 90°$ and exposition was 10 s per point. Morphologies and microstructures of as-prepared samples were analyzed by a JSM-6390LV scanning electron microscopy (SEM).

During the MW and thermal heating processes, the composition of gas mixture and partial pressures P_i of components were controlled by an IPDO-2 mass-spectrometer.

3. Results and Discussion

3.1 Interaction of Cadmium and Zinc Nitrates with the Ammonium Paratungstate

During heating of the mixture of cadmium and zinc nitrates with ammonium paratungstate, a liquid phase formed at 100 °C, related to the dissolution of the initial components in their own crystalline water. Increasing the temperature from 100 to 200 °C resulted in an intense evaporation of water and this process began as early as 30-60 s after the start of MW irradiation. The emission of nitrogen began after increasing temperature over 250 °C. An intensive extraction of nitrogen oxides was observed in 3-4 min after starting the irradiation, when the temperature was 350 °C and it was completely finished at 450 °C. The samples for IR measuring were selected from different stages of synthesis. For control points we selected the following temperatures: 100, 200, 300, and 400 °C. After final cooling, white color powders were obtained.

The results of scanning microscopy are presented in Fig. 1. According to these results, during synthesis of zinc (Fig. 1a, b) and cadmium (Fig. 1c, d) tungstates by MW heating, agglomerates are formed, consisting of spherical particles with size 20-50 nm.

The FT-IR spectra for $CdWO_4$ in the initial state and after heat treatment at 100-450 °C are shown in Fig. 2. For the initial sample (Fig. 2a) we can see the peaks at 3000-3600 cm^{-1} (O-H band of crystallization water) and 1640 cm^{-1} (O-H alcohol band), 1380 and 825 cm^{-1} (NO_3^- bands) and the absorption peaks near 940, 690, 595, 512 cm^{-1} (paratungstate bands). At 200 °C the bands of the OH^- group decrease, while new absorption bands appear between 500 and 900 cm^{-1} (Fig. 2b). The bands of Cd-O (595 cm^{-1}), W-O (690 cm^{-1}), and Cd-O-W (800, 870 cm^{-1}) (Fig. 2c-e) can be identified as synthesized $CdWO_4$. At 450 °C the bands of the NO_3^- group and O-H groups disappear (Fig. 2e).

Thus, formation of cadmium (Fig. 2) and zinc (Fig. 3) tungstate begins already in the initial stages of heating at melting of initial hydrates and it is completed at 400-450 °C after their decomposition.

The mass-spectrometry results for the gas atmosphere composition for a cadmium or zinc salts mixture were practically identical and the case of cadmium nitrate is illustrated in Fig. 4, as an example.

During heating of initial mixture at the temperature interval of 25-300 °C and above 400 °C water, connected with

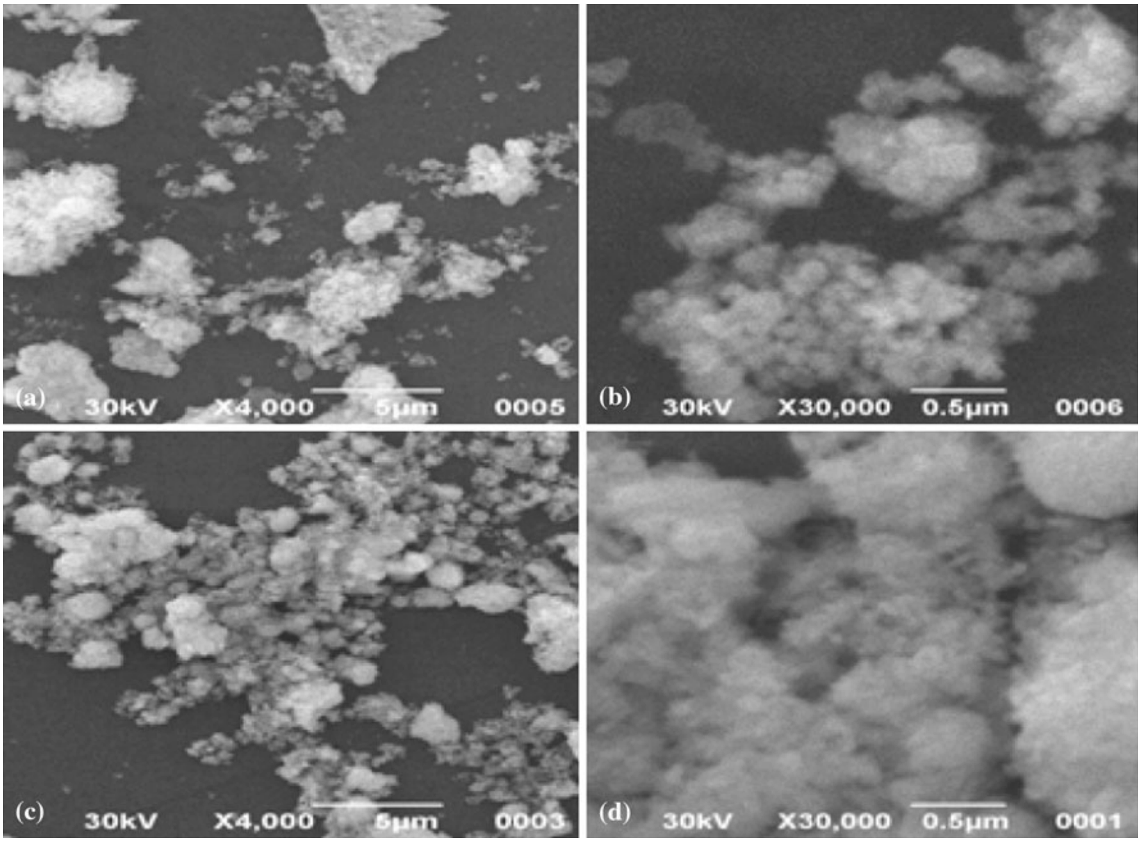

Fig. 1 SEM images of $ZnWO_4$ (a, b) and $CdWO_4$ (c, d) obtained by decomposition of metal nitrates and ammonium paratungstate mixture using MW

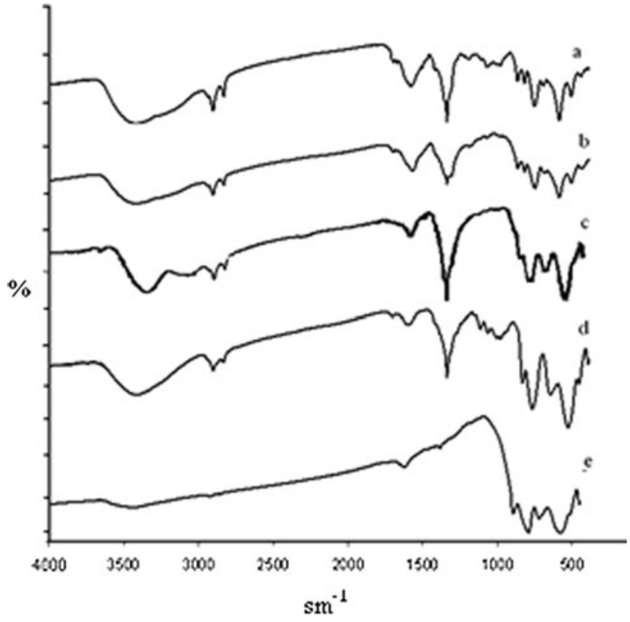

Fig. 2 IR spectra of the sample that were obtained by MW heating of mixture of cadmium nitrates and ammonium paratungstate at temperatures: (a) 20 °C, (b) 100 °C, (c) 200 °C, (d) 350 °C, (e) 450 °C

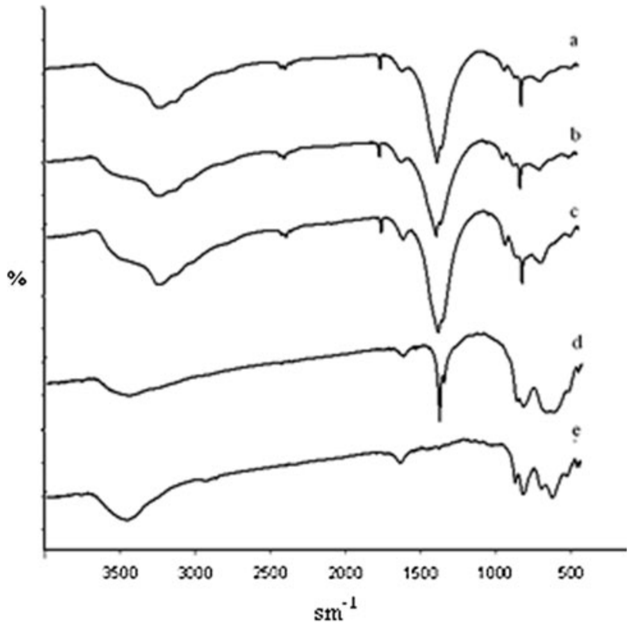

Fig. 3 IR spectra of the sample that were obtained by MW heating of mixture of zinc nitrates and ammonium paratungstate at temperatures: (a) 20 °C, (b) 100 °C, (c) 200 °C, (d) 350 °C, (e) 450 °C

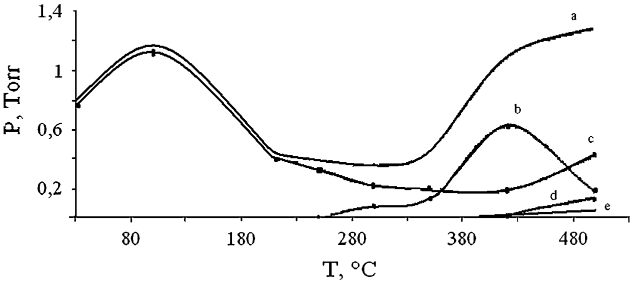

Fig. 4 Temperature variation of total pressure (a) and partial pressures of H_2O (b), NO (c), NO_2 (d), and N_2O (e) during heating of cadmium nitrate and ammonium paratungstate mixture

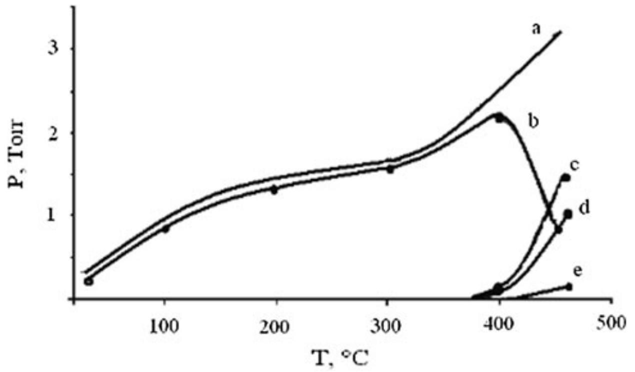

Fig. 5 Temperature variation of total pressure (a) and partial pressures of H_2O (b), NO (c), O_2 (d), and NO_2 (e) during heating of cadmium nitrate

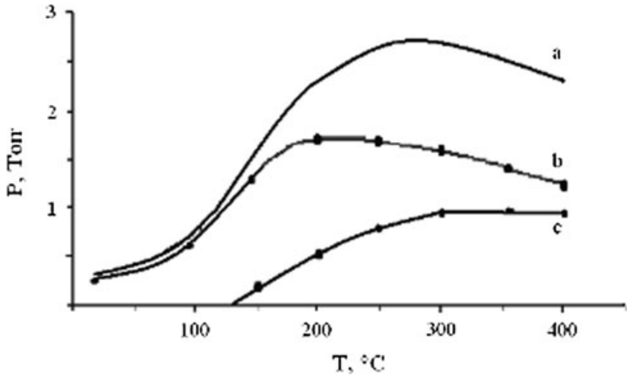

Fig. 6 Temperature variation of total pressure (a) and partial pressures of H_2O (b) and NH_3 (c) during heating of ammonium paratungstate

decomposition of initial hydrates, was released (Fig. 4b). At temperatures higher than 250 °C there was emission of NO and N_2O, and at temperatures higher than 400 °C—NO_2. The presence of nitrous oxides in the decomposition mixture can testify to the formation of ammonium nitrate, which is connected with the N_2O emission. Studying the thermal decomposition of cadmium nitrate only, the emission of N_2O was not observed (Fig. 5) but emission of NO, O_2, and NO_2 took place. The emission of N_2O during thermal decomposition of ammonium paratungstate $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ was not observed either (Fig. 6), however, emission of NH_3 and H_2O took place. Thus, the emission of N_2O during heating of the mixture of cadmium nitrate and ammonium paratungstate was probably related to the decomposition of ammonium nitrate that appears as a reaction product of ammonium paratungstate and metal nitrate.

The XRD analysis of synthesized $CdWO_4$ powder has revealed the presence of monoclinic phase (a = 5.034 Å, b = 5.854 Å, c = 5.074 Å, β = 91.570°) and also of an unknown phase. Identification of unknown phase lines has shown that it demonstrates tetragonal symmetry. The primary search of phases is executed using card index PDF-1 (Ref 21) and calculation was executed with the Rietveld method

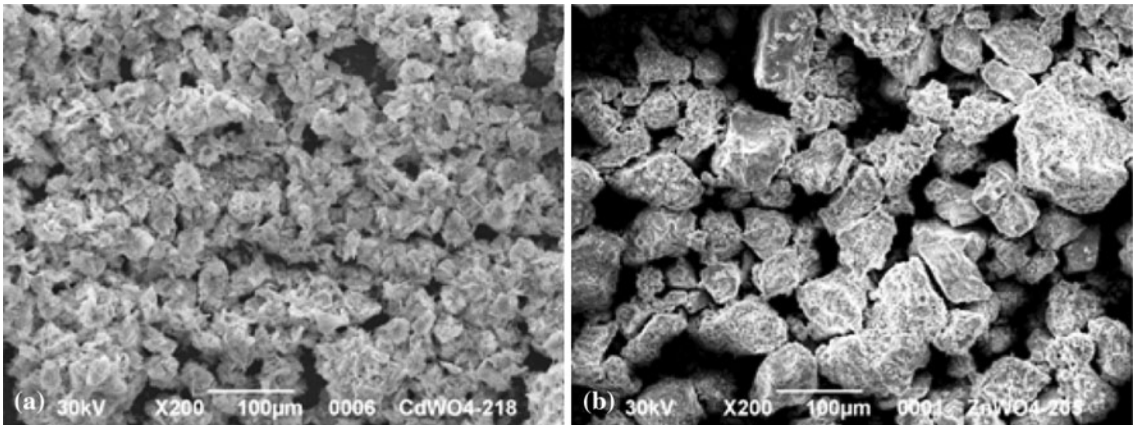

Fig. 7 SEM images of $CdWO_4$ (a) and $ZnWO_4$ (b) obtained by thermal heating of nitrates metals and ammonium paratungstate mixture

(Ref 22, 23) using FullProf (Ref 24). Verification of structure model with the Rietveld method has shown that the unknown phase was cadmium tungstate, forming scheelite structure ($I4_1/a$, a = 5.170 Å, c = 11.140 Å).

The XRD analysis of synthesized $ZnWO_4$ powder by MW method has revealed the presence of only the standard monoclinic phase.

3.2 Interaction of Cadmium and Zinc Nitrates with Ammonium Paratungstate During Thermal Heating

During thermal heating of mixture of metal nitrate and ammonium paratungstate the characteristics of cadmium and zinc tungstates synthesis have remained the same as in the case of MW activation but the synthesis time was more 30 min. During heating of mixture in the temperature range of 25-300 °C and above 400 °C, the emission of water was observed. At temperatures higher than 250 °C, there was emission of NO and N_2O. The emission of NO_2 was fixed at temperatures more 400 °C. The emission of N_2O in both MW and thermal types of activating is characteristic of the total mechanism of cadmium and zinc tungstates formation. The XRD analysis of synthesized powders has shown the presence of monoclinic $CdWO_4$ and monoclinic $ZnWO_4$. The cadmium tungstate with tetragonal symmetry was not obtained.

The results of scanning microscopy investigations are presented in Fig. 7. According to the obtained results, during synthesis of cadmium (Fig. 7a) and zinc (Fig. 7b) tungstates by thermal heating, microcrystals of sizes 50-100 µm were formed.

In this case, the interaction between cadmium or zinc nitrates and ammonium paratungstate begins already in a liquid phase, after the melting of initial hydrates and flows according to the following general reaction:

$$\begin{aligned}&12\mathrm{Me(NO_3)_2{\cdot}4H_2O} + \mathrm{(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O}\\&\xrightarrow{T,^\circ\mathrm{C}} 12\mathrm{MeWO_4} + 10\mathrm{(NH_4)NO_3} + 11\mathrm{NO}\uparrow\ + 3\mathrm{NO_2}\uparrow\\&\quad + 9\mathrm{O_2}\uparrow + 53\mathrm{H_2O}\uparrow \qquad \text{(Eq 1)}\end{aligned}$$

$$\mathrm{(NH_4)NO_3} \xrightarrow{T,^\circ\mathrm{C}} \mathrm{N_2O}\uparrow\ + 2\mathrm{H_2O}\uparrow \qquad \text{(Eq 2)}$$

$$\begin{aligned}&12\mathrm{Me(NO_3)_2{\cdot}4H_2O} + \mathrm{(NH_4)_{10}W_{12}O_{41}\cdot 6H_2O}\\&\xrightarrow{T,^\circ\mathrm{C}} 12\mathrm{MeWO_4} + 10\mathrm{N_2O}\uparrow\ + 11\mathrm{NO}\uparrow\ + 3\mathrm{NO_2}\uparrow\\&\quad + 9\mathrm{O_2}\uparrow\ + 73\mathrm{H_2O}\uparrow \qquad \text{(Eq 2)}\end{aligned}$$

where Me = Cd, Zn

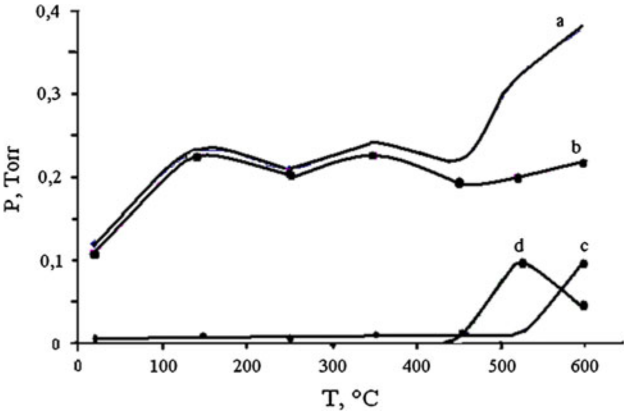

Fig. 8 Temperature variation of total pressure (a) and partial pressures of H_2O (b), N_2 (c), and CO_2 (d), during heating of $ZnWO_4$, synthesized by MW

As a result, at a temperature of 400-450 °C in the system, a unique product—cadmium tungstate—was generated. All other products decompose with formation of gaseous components (nitrogen oxides and water). It should be noted that the MW activation promotes and accelerates the interaction between the initial components. Thus, the time at the end of gases emission during traditional thermal heating of metal nitrate and ammonium paratungstate mixture was 30 min, while for MW heating—7-10 min.

To estimate the completeness of interaction between the initial components we performed a test of thermodesorption at heating to 800 °C.

Mass-spectrometry results for $ZnWO_4$ and $CdWO_4$ that were synthesized by MW heating are presented in Fig. 8 and 9, respectively. For heating to 600 °C, the basic emission component was water that adsorbed from the surface of metal tungstate particles. Also there is thermodesorption of CO_2 (not shown) in the temperature range of 450-600 °C and emission of N_2 at a temperature higher than 500 °C.

The history of receipt salts and preliminary thermal heating did not have influence on the character of N_2 emission that was practically constant (Fig. 10c). The N_2 emission likely was the result of N_2 desorption from the cadmium tungstate particle surface. An absence of ammonium and nitrogen oxides from the system should be noted, which testifies to complete decomposition of the initial components.

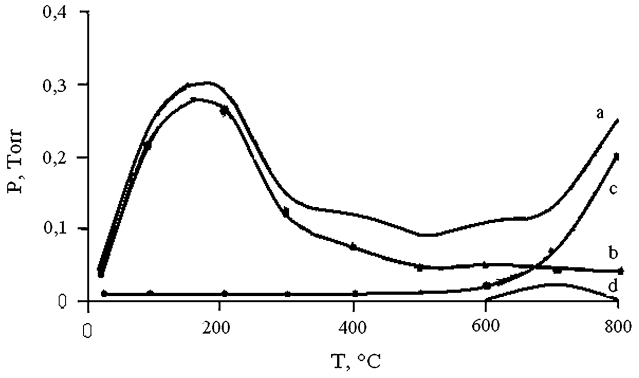

Fig. 9 Temperature variation of total pressure (a) and partial pressures of H_2O (b), N_2 (c), and CO_2 (d), during heating of $CdWO_4$, synthesized by MW

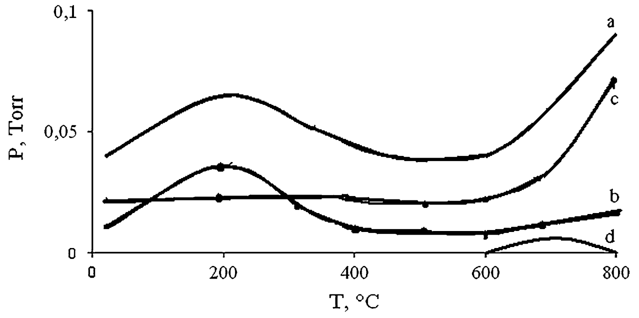

Fig. 10 Temperature variation of total pressure (a) and partial pressures of H_2O (b), N_2 (c), and CO_2 (d), during heating of $CdWO_4$ that was synthesized by thermal heating

4. Conclusions

Summarizing the main features of the results reported pertaining to MW synthesis of cadmium and zinc tungstates, the following concluding remarks may be drawn:

- The investigation of zinc or cadmium nitrates and ammonium paratungstate interaction indicated the possibility of effectively obtaining metal tungstates by MW radiation. These reactions begin at the melting point of crystallohydrates (100 °C) and finish at the complete decomposition of mixture (400-450 °C) with tungstate formation. The MW activation essentially does not influence the mechanism of cadmium or zinc nitrates and ammonium paratungstate reaction. The MW activation allows accelerating reactions (by 3-5 times) in comparison with traditional heating methods.
- During the MW activation of the interaction between cadmium nitrate and ammonium paratungstate, cadmium tungstate with the scheelite structure is formed. This phase does not appear during thermal heating of the same reaction mixture.

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