

## THULIUM-CONTAINING HETEROPOLY TUNGSTATE WITH PEACOCK-WEAKLEY ANION: SYNTHESIS, PROPERTIES, AND SURFACE MICROMORPHOLOGY

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The conditions for the synthesis of novel sodium heteropoly decatungstothuliate (III)  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$  from an aqueous solution of sodium tungstate acidified to  $Z=0.80$  with a ratio  $v(\text{Tm}):v(\text{W})=1:10$  and with acetone admixture were elaborated. By means of FTIR spectroscopy, we showed that the heteropoly anion contained in the isolated salt has a Peacock-Weakley structure. Thulium nitrate and sodium heteropoly decatungstothuliate (III) solutions were analyzed using UV-Vis spectroscopy, and a bathochromic shift in the heteropoly salt solution was established that is caused by the change in coordination polyhedron of Tm (III) ion during transition from aqua complex to Peacock-Weakley heteropolyanion with coordination towards the heteroatom of lacunar pentatungstate anions in the form of square antiprisms. Using scanning electron microscopy, the morphology of heteropolycompound surface was studied; it was stated that the grain size is within the range of 200–350 nm. The single-phase condition of the synthesized salt was confirmed by the surface uniform contrast in backscattered electron mode. DTA method was used to study the thermal decomposition of the salt, while XRF analysis revealed the formation of sodium ditungstate and double sodium-thulium orthotungstate as a result of thermolysis.

**Keywords:** thulium, heteropoly tungstate, Peacock-Weakley structure, surface micromorphology.

### Introduction

Nowadays there are two groups of lanthanide-containing polyoxotungstates made of lacunar isopolytungstate anions [1]. The first one includes heteropolytungstolanthanides of 10th row with Peacock-Weakley anion  $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$  (Ln – La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Y), in which two lacunar pentatungstate anions  $\text{W}_5\text{O}_{18}^{6-}$ , derived from the Lindqvist structure  $\text{W}_6\text{O}_{19}^{2-}$ , are coordinated to heteroatom [2–6]. The second one includes 11th row compounds



(Ln=La, Ce, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) with Keggin-type lacunary metatungstate anion [7]. It bears mentioning that in spite of available publications highlighting the synthesis and properties of lanthanide heteropoly decatungstate (III) with Peacock-Weakley type anion, there is no single research paper dedicated to obtaining of thulium (III)-containing heteropolytungstate of 10th row. There is only information about two compounds, in which  $\text{Tm}^{3+}$  ions are located in the outer sphere of polyoxotungstate anion –  $\text{Na}_8[\text{Tm}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{72}(\text{OH})_2] \cdot 41\text{H}_2\text{O}$  [7] and  $[\text{Tm}_2(\text{H}_2\text{O})_{14}\text{CrMo}_6\text{O}_{24}\text{H}_6][\text{CrMo}_6\text{O}_{24}\text{H}_6] \cdot 16\text{H}_2\text{O}$  [8], while compounds with  $\text{Tm}^{3+}$  ions in the role of

heteroatoms are not described in the literature.

As stated in [9], most of the currently known polyoxometallates are synthesized by self-assembly in solutions with mononuclear initial components. This is a particular type of synthesis, when several different reactions between different reagents simultaneously occur in the system, resulting in a final product with complex structure. Direction of the reaction is often determined by subtle differences in structure and reactivity of intermediates. And the most important factor that affects the reaction mechanism is complementarity of fragments compounding the final product.

The paper presents the results of synthesis of a previously undescribed heteropoly compound with Peacock-Weakley type anion  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \times 33\text{H}_2\text{O}$ , which was carried out by the self-assembly from  $\text{WO}_4^{2-}$  and  $\text{Tm}^{3+}$  in an acidified aqueous solution; it also studies its properties by FTIR and UV-Vis spectroscopy, thermal and X-ray diffraction analysis, scanning electron microscopy. The paper describes the technique of synthesis developed and used to obtain a neutral salt that will allow isolating in future heteropoly compounds  $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot n\text{H}_2\text{O}$  with other Ln-heteroatoms.

### Experimental Part

*Characteristics and standardization of initial*

*substances*

Sodium tungstate solution  $\text{Na}_2\text{WO}_4$  was prepared by dissolving  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (analytically pure grade) in distilled water. The exact concentration ( $C_w=0.4953$  mol/L) was determined gravimetrically (in the form of  $\text{WO}_3$ ,  $d=0.5\%$ ) according to the method described in [10]. Nitric acid solution ( $C=0.4832$  mol/L) was prepared from the concentrated  $\text{HNO}_3$  (chemically pure grade). The exact concentration was determined by titrating a weighed amount of sodium tetraborate (methyl red indicator) ( $d=0.5\%$ ) [11]. Recrystallized sodium tetraborate decahydrate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  was used for standardization purpose; water content in it was determined gravimetrically based on the weight loss after isothermal calcination ( $500^\circ\text{C}$ ) [11]. The solution  $\text{Tm}(\text{NO}_3)_3$  ( $C=0.1254$  mol/L) was prepared by dissolving  $\text{Tm}_2\text{O}_3$  (Technical specifications 48-4-182-72) in  $\text{HNO}_3$ . Excess amount of  $\text{HNO}_3$  was removed by two-fold evaporation until wet residue was formed, which then was dissolved in distilled water. Concentration of  $\text{Tm}(\text{III})$  was determined by direct complexometric titration using Trilon B solution (analytically pure grade) in acetate buffer solution with pH 5.5 (74.8 g of  $\text{CH}_3\text{COONa} \cdot 3\text{N}_2\text{O}$  (analytically pure grade), 1 fixanal of  $\text{CH}_3\text{COOH}$ ) (xylenol orange indicator) ( $d=0.8\%$ ) [12]. Acetone  $\text{CO}(\text{CH}_3)_2$  (analytically pure grade) was used to isolate sodium heteropoly decatungstothuliate (III).

*Technique of salt synthesis*

The synthesis of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$  was carried out as following. Sodium tungstate solution (20.19 mL,  $C=0.4953$  mol/L) was added to 55.28 mL of distilled water, and then  $\text{HNO}_3$  solution (16.56 mL,  $C=0.4832$  mol/L) was added dropwise with vigorous stirring. After that  $\text{Tm}(\text{NO}_3)_3$  solution (7.97 mL,  $C=0.1254$  mol/L) was added dropwise very slowly with vigorous stirring. It bears mentioning that each next drop of  $\text{Tm}(\text{NO}_3)_3$  was added only after the disappearance of opalescence from the previous drop. The volume of the final aqueous solution amounted to 100 mL. Adding of reactants in the above-mentioned amounts corresponds to the stoichiometry of the reaction, during which heteropoly decatungstothuliate (III) anion is formed [2,5]:



In order to isolate the resulting anion from the salt as a precipitate, 100 mL of acetone (analytically pure grade) was added to the solution. Then, the resulting product was sealed and stored for 3 days at  $6^\circ\text{C}$  that led to the formation of acicular crystalline precipitate.

*Methods of chemical analysis*

To carry out chemical analysis, exact weighed

amounts ( $\sim 0.2000$  g each) of air-dry sample were heated in a mixture of concentrated  $\text{HCl}$  and  $\text{HNO}_3$  (15 and 5 mL, respectively) in order to convert tungsten to an insoluble precipitated  $\text{WO}_3 \cdot x\text{H}_2\text{O}$  and partially separate it from sodium and thulium. To completely separate sodium and thulium after evaporation, 10 mL of  $\text{HNO}_3$  was added to the wet precipitate and evaporated on a steam bath nearly to dryness. Then 70 mL of distilled water was added and evaporated to 40 mL on a water bath.  $\text{WO}_3 \cdot x\text{H}_2\text{O}$  precipitate then was filtered using Blue Ribbon ashless filter, washed with 3% solution of  $\text{HNO}_3$ , dried, and calcinated at  $800^\circ\text{C}$  to form  $\text{WO}_3$  ( $\delta=0.5\%$ ) [10]. In the collected filtrate  $\text{Tm}^{3+}$  and  $\text{Na}^+$  contents were determined.

To determine  $\text{Tm}^{3+}$  contents, direct complexometric titration was carried out [12]. For this, the filtrate was evaporated nearly to dryness, then distilled water was added to obtain a final volume of 100 mL and an aliquot (1.00 mL) was collected to determine sodium content. The remaining solution was evaporated to 20 mL, and 30 mL of acetate buffer solution (pH 5.5) was added in it. Thereafter, titration was carried out using Trilon B solution ( $C=0.0250$  mol/L). Equivalence point was fixed visually when xylenol orange indicator changed its color from pink to yellow. The sodium content in the filtrate was determined by atomic absorption spectroscopy. The water content in the salts was determined by calcinating of exact weighed amounts (each 0.1500 g) of air-dry sample at  $550^\circ\text{C}$  ( $\delta=0.5\%$ ).

Chemical Anal. Calcd (wt. %) for the white crystals of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$ :  $\text{Na}_2\text{O}$  8.24;  $\text{Tm}_2\text{O}_3$  5.70;  $\text{WO}_3$  68.50;  $\text{H}_2\text{O}$  17.56; found (wt. %):  $\text{Na}_2\text{O}$  8.3;  $\text{Tm}_2\text{O}_3$  5.9;  $\text{WO}_3$  68.4;  $\text{H}_2\text{O}$  17.5. Yield 90%.

*Instrumental methods of analysis*

*FTIR spectroscopy*

FTIR-spectroscopy was used to identify anion in the synthesized salt. FTIR spectrum of the air-dry sample of salt was recorded on FTIR Spectrum BXII (Perkin-Elmer), within the wavenumber range of  $400\text{--}4000$   $\text{cm}^{-1}$ . For this, a weighed amount of salt (0.0030 g) was triturated with monocrystalline KBr (0.6000 g) and compressed into a thin disk.

*X-ray diffraction (XRD)* was carried out using powder diffraction technique on DRON-3 ( $\text{CuK}_\alpha$  radiation, Ni-filter). Diffraction patterns were recorded in the areas of Bragg angles  $6^\circ < 2\theta < 66^\circ$ .

*Microscopic analysis*

Microscopic research was conducted by scanning electron microscopy (SEM) with microscope JSM-6490LV (JEOL). Air-dry sample deposited on a conductive graphite scotch tape was studied in backscattered electron (BEC) mode used for the elemental analysis of phases being the parts of the sample, and in secondary electron (SEI) mode used to study the surface of the resulting salt.

Elemental analysis during the microscopic studies was performed with energy-dispersive X-ray spectrometer INCA PentaFETx3 (OXFORD Instruments).

*Differential thermal analysis (DTA)* was performed with derivatograph Q1500D in the mode of linear temperature rise within the range of 25–700°C. The rate of temperature increase was 5°C/min; the sample was kept in a ceramic crucible without a lid.

*Atomic absorption spectroscopy*

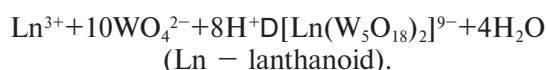
Determination of Na(I) content in the salt ( $\delta=2\%$ ) was performed with atomic absorption spectrometer «Saturn 3» in air/acetylene flame at analytical line of 589.6 nm using a high-frequency electrodeless lamp VSB-2 as a source of resonance radiation (current  $I=70$  mA).

*Electron spectroscopy*

Analysis of the state of complexes in aqueous solution was performed with a double-beam spectrophotometer Specord 200 (Analytik Jena) in the range  $\lambda=200-1100$  nm. Solutions were placed in quartz cuvettes with 10 mm thickness of the absorbing layer, and then UV-Vis spectra were recorded against distilled water. The assignment of electron states within the absorption spectrum was made on the basis of the data [13].

**Results and their Discussion**

Acidity  $Z=v(H^+)/v(WO_4^{2-})=0.80$  in the presence of stoichiometric amounts of reactive ions corresponds to the formation of heteropoly decatungstolanthanidate (III) anions [5]:



To isolate such particles with Tm(III) ions-heteroatoms, sodium tungstate solution ( $C_w=0.1$  mol/L) acidified to  $Z=0.80$  was used, to which  $Tm(NO_3)_3$  solution was added with vigorous stirring. After decanting of the components in a stoichiometric ratio of  $Tm:W=1:10$ , acetone was added to the system (up to 50 vol. %) and formation of acicular crystalline precipitate was observed. Product yield was ~90%; loss amounting to ~10% was most likely caused by the solubility of salt when washing the precipitate with water-acetone mixture (1:1) during its separation from the mother liquor. According to the results of the chemical analysis and FTIR spectroscopy (Fig. 1, Tab. 1) the isolated precipitate was assigned the formula  $Na_9[Tm(W_5O_{18})_2] \cdot 33H_2O$ .

Nature of stretch and deformation vibrations in the tungsten-oxygen framework within FTIR spectrum of air-dry sample of salt (Fig. 1, Table 1) indicates to the presence of Peacock-Weakley heteropoly anion of 10th row in it [5,6]. In this anion, two lacunar tetradentate pentatungstate-anions  $W_5O_{18}^{6-}$  are coordinated to Tm-heteroatom, thus

forming a coordination polyhedron in the shape of a square antiprism.

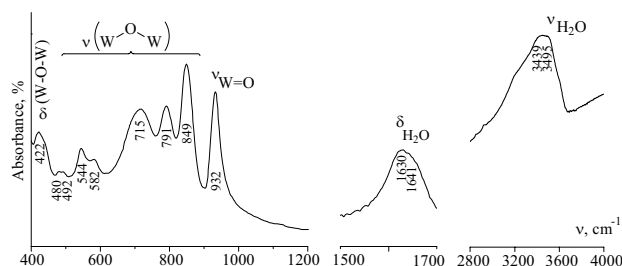


Fig. 1. FTIR-spectrum of  $Na_9[Tm(W_5O_{18})_2] \cdot 33H_2O$

Table 1  
Absorbance wave frequencies in FTIR spectra of salts with  $[X(W_5O_{18})_2]^{9-}$  anion

X	$\delta(W-O-W)$	$\nu(W-O-W)$						$\nu(W=O)$
Tm	422	492	544	582	715	791	849	932
Nd*	421	500	542	598	724	794	852	943
Y**	422	490	547	615	707	782	845	940

Note: Tm –  $Na_9[Tm(W_5O_{18})_2] \cdot 33H_2O$ , synthesized in this work; Nd\* –  $Tl_8H[Nd(W_5O_{18})_2] \cdot 7H_2O$  [5]; Y\*\* –  $Na_9[Y(W_5O_{18})_2] \cdot 35H_2O$  [6].

It bears mentioning that there are two most commonly used methods of heteropoly decatungstolanthanidate (III) synthesis as of today. The first one was proposed in 1971 by R.D. Peacock and T.J.R. Weakley [2], and the heteropoly anion  $[X(W_5O_{18})_2]^{9-}$  was named after them. According to the method,  $Na_2WO_4$  solution is acidified with acetic acid to pH 7.0–7.2, and solutions of lanthanide nitrates or chlorides are added in it at  $T=90^\circ C$  with vigorous stirring. Crystalline precipitate is formed either as a result of slow crystallization at room temperature, or by cooling the solution to 5°C. In both cases, the salts obtained in [2] are acidic  $M_7H_2[Ln(W_5O_{18})_2] \cdot nH_2O$  ( $M=K, Cs, CH_6N_3$ ;  $Ln=Ce, Y, La, Pr, Nd, Sm, Eu, Ho, Er, Yb$ ;  $n=8-17$ ). According to the second method [5], the desired pH in the solution is achieved by introducing an acetate buffer solution and thallium nitrate in it. A method described in [5] made it possible to isolate salts with required number of protons  $Tl_{(9-n)}H_n[Ho(W_5O_{18})_2] \cdot mH_2O$  ( $n=2-4$ ;  $m=7-9$ ). Thus, the method for obtaining sodium heteropoly decatungstothuliate (III), described in this paper, is a new one and it allows to synthesize a neutral salt with Peacock-Weakley heteropoly anion.

UV-Vis spectroscopy was used to obtain electronic absorption spectra for solutions of nitrate thulium and sodium heteropoly decatungstothuliate (III)  $Na_9[Tm(W_5O_{18})_2] \cdot 33H_2O$  (Fig. 2) with concentration of  $C(Tm^{3+})=0.05$  mol/L.

In the electronic absorption spectrum of sodium heteropoly decatungstothuliate (III) solution a bathochromic shift is observed, which may be caused

by the changes in the ligand environment (coordination polyhedron) of lanthanide ion in aqueous solution (spherical aquacomplex) during the formation of Peacock-Weakley heteropoly anion (square antiprism). The nature of differences in UV-Vis spectrum and changes in the position of absorption maxima may indicate an absence of dissociation of the anion  $[\text{Tm}(\text{W}_5\text{O}_{18})_2]^{9-}$  into  $\text{Tm}^{3+}$  and  $\text{W}_5\text{O}_{18}^{6-}$  in sodium heteropoly decatungstothuliate (III) solution. In addition, the presence of electronic transition  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  at  $\lambda = 800$  nm might be interesting to use  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$  in laser applications [14].

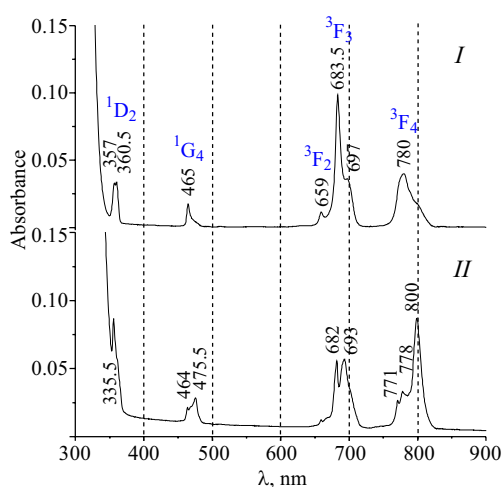


Fig. 2. Electronic absorption spectra of the solutions: I –  $\text{Tm}(\text{NO}_3)_3$ ; II – sodium heteropoly decatungstothuliate (III);  $+C(\text{Tm}^{3+})=0.05$  mol/L

During thermolysis of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$  several temperature ranges of mass loss are fixed on TG and DTG curves of the thermogram (fig. 3), that is also reflected in the form of endo-effects on DTA curve: 40–75–100°C, 100–110–150°C, 150–335°C. These endo-effects are caused by dehydration of heteropoly compound.

The number of moles of  $\text{H}_2\text{O}$ , lost at various stages of dehydration, is given in Table 2.

TG curve (Fig. 3) demonstrates that the mass loss occurs up to the temperature of 335°C, while further heating leads to the appearance of exo-effect on DTA curve (420–440°C), which corresponds to crystallization of sodium ditungstate  $\text{Na}_2\text{W}_2\text{O}_7$  and double sodium-thulium orthotungstate  $\text{Na}_{0.5}\text{Tm}_{0.5}\text{WO}_4$ ;

their reflections are fixed on X-ray diffraction pattern of the thermolysis products (Fig. 4).

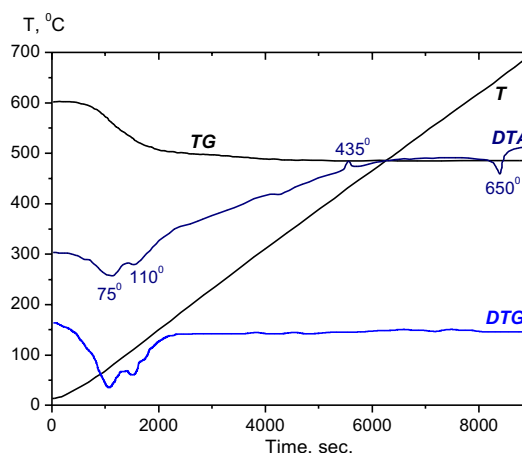
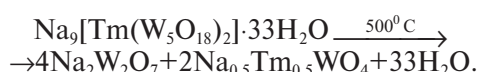


Fig. 3. Thermogram of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$  (Curves: T – for temperature, TG – thermogravimetric, DTG – differential thermogravimetric, DTA – differential thermal analysis)

X-ray diffraction analysis of the crystalline precipitate  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$  was carried out, but it was impossible to compare the resulting X-ray diffraction pattern (Fig. 4,a) with an analogue in ICDD database [15] because there is no such a phase in it. In addition, the X-ray diffraction pattern of thermolysis products (2 hours, 500°C) demonstrates reflections of  $\text{Na}_2\text{W}_2\text{O}_7$  (ICDD PDF 01–070–0860 [15]) and  $\text{Na}_{0.5}\text{Yb}_{0.5}\text{WO}_4$  (ICDD PDF 00–025–0887 [15]) (Fig. 4,b) that allows to propose a thermolysis scheme for  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$ :



It bears mentioning that X-ray diffraction pattern of thermolysis products being calcinated at a higher temperature (2 hours, 800°C) contains reflections of the same phases as after calcination at 500°C (Fig. 4,c). This indicates the absence of any further decomposition or any further interaction between the thermolysis products, and makes it possible to conclude that the endo-effect, fixed on DTA curve at 650°C (Fig. 2), is caused by melting of the thermolysis products.

Table 2

**Results of thermogravimetric analyses for  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$**

Temperature range, °C	Experimental weight loss, wt. %	Calculated weight loss, wt. %	Moles of lost water per each $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 33\text{H}_2\text{O}$
40–75–100	9.8	9.58	18
100–110–150	5.7	5.85	11
150–335	2.0	2.13	4



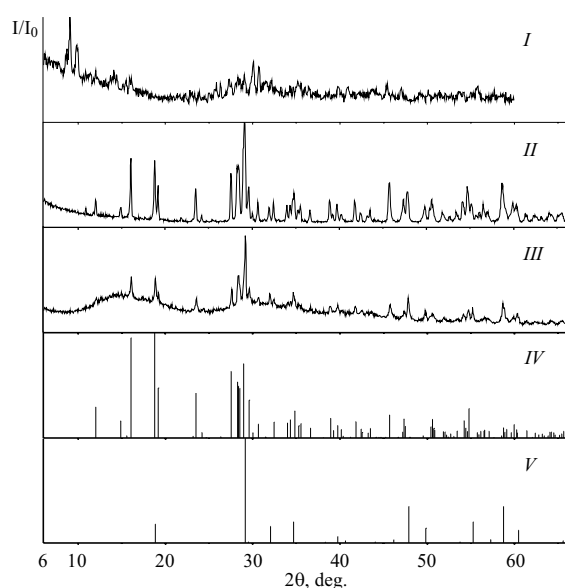


Fig. 4. X-ray diffraction patterns: I –  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  (air-dry); II – thermolysis products of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  (2 hours at  $500^\circ\text{C}$ ); III – thermolysis products of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  (2 hours at  $800^\circ\text{C}$ ); IV –  $\text{Na}_2\text{W}_2\text{O}_7$  (ICDD PDF 01-070-0860 [15]); V –  $\text{Na}_{0.5}\text{Yb}_{0.5}\text{WO}_4$  (ICDD PDF 00-025-0887 [15])

Thermolysis also leads to the formation of  $\text{Na}_{0.5}\text{Tm}_{0.5}\text{WO}_4$  phase, absent in the ICDD database, which is isostructural  $\text{Na}_{0.5}\text{Yb}_{0.5}\text{WO}_4$  (ICDD PDF 00-025-0887 [15]) due to close ionic radii of lanthanide cations [16] and the position of reflections in the diffraction pattern.

Nowadays, microscopic studies represent an effective mechanism to determine single-phasesness of synthesized salts, when this is not possible by using X-ray diffraction. In [17] X-ray analysis revealed the formation of a mixture of three polyoxotungstates in the system  $\text{Ln}^{3+}-\text{WO}_4^{2-}-\text{H}^+-\text{H}_2\text{O}$  ( $\text{Ln}=\text{Tb}, \text{Gd}$ ) during the preparation of compounds with Peacock-Weakley anion: major product  $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2]\cdot x\text{H}_2\text{O}$ , and minor impurities  $\text{Na}_{12}\text{H}[(\text{W}_5\text{O}_{19})\text{Ln}(\text{H}_2\text{W}_{11}\text{O}_{39})]\cdot 42\text{H}_2\text{O}$  and  $\text{Na}_{10}[\text{W}_{12}\text{O}_{40}(\text{OH})_2]\cdot n\text{H}_2\text{O}$ . In earlier publications [2] it was considered that the salt with Peacock-Weakley anion was the only product resulted from the synthesis.

Microscopic analysis showed that the surface of grains in the isolated salt  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  has fuzzy blurred edges. The grain size of the sample is within the range of 200–350 nm (Fig. 5).

Uniform surface contrast in BEC mode points to single-phasesness of the salt obtained (Fig. 6).

On the micrographs of  $\text{Na}_9[\text{Dy}(\text{W}_5\text{O}_{18})_2]\cdot 30\text{H}_2\text{O}$  powder in characteristic X-ray emission there are no regions with different surface morphology, and there is an even distribution of Tm, Na, W, O,

without segregation and eliquation (apparent heterogeneities are explained by different relief of the sample surface) (Fig. 7). These clearly indicate the formation of monophas sample.

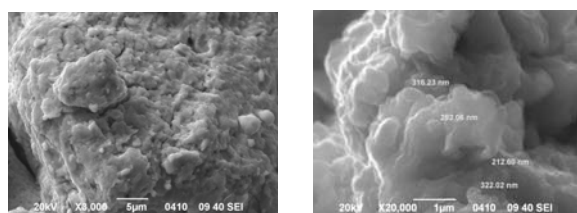


Fig. 5. SEM image of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  powder surface: left – 3,000 times magnification; right – 20,000 times magnification

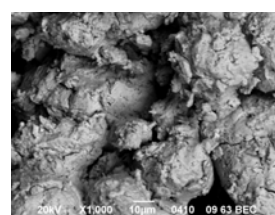


Fig. 6. Image of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  powder surface: in backscattered electron mode

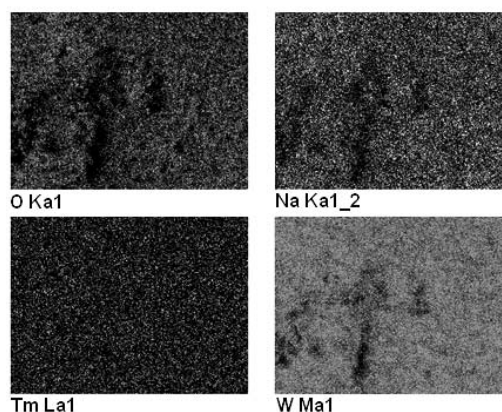
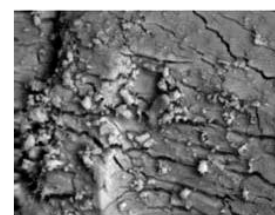


Fig. 7. Image of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  powder surface during characteristic X-ray emission (Tm  $L_{\alpha 1}$ , Na  $K_{\alpha 1-2}$ , W  $M_{\alpha 1}$ , O  $K_{\alpha 1}$ )

X-ray spectral microanalysis was carried out in various areas of the powder surface having different squares (from  $8.1\times 9.1$  to  $63.5\times 47.6$   $\text{mm}^2$ ). The results of elemental analysis (Fig. 8, Table 3) are identical to the results of classical chemical analysis and for  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  the molar ratio of elements

Tm:Na:W=1.00:8.98:9.97 (theoretical ratio Tm:Na:W=1.00:9.00:10.00).

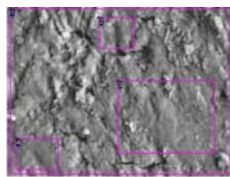


Fig. 8. SEM image of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  powder: areas, in which elemental analysis was carried out, are shown (see Table 3)

Table 3  
Atomic ratio of Na, Tm, and W in different surface zones of trituated  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$

W, at. %	Zones					$V_{\text{Na}}:V_{\text{Tm}}:V_{\text{W}}$	
	1	2	3	4	Average	Exp.	Theor.
Na	12.45	12.11	12.28	12.01	12.21	8.96	9
Tm	1.38	1.35	1.37	1.35	1.36	1	1
W	13.77	13.62	13.51	13.49	13.60	9.98	10

Thus, in the paper we described the conditions, under which the formation and synthesis of the previously undescribed heteropoly compound  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  occurs; also we investigated its composition and properties by applying the complex of physical-chemical and physical methods of analysis – FTIR spectroscopy, UV-Vis spectroscopy, XRD, DTA, SEM.

#### Conclusions

1. The conditions for the synthesis of a new thulium-containing heteropolytungstate  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  from the aqueous solution, acidified to  $Z=n(\text{H}^+)/n(\text{WO}_4^{2-})=0.80$  with acetone adding, were determined. FTIR spectroscopy was used to show that the anion within the synthesized salt has a Peacock-Weakley structure. The method for obtaining sodium heteropoly decatungstothuliate (III), described in this paper, is a new one and it allows to synthesize a neutral salt; in future this can be used in synthesis of neutral salts  $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2]\cdot n\text{H}_2\text{O}$  with other Ln-heteroatoms.

2. UV-Vis spectroscopy of thulium nitrate and sodium heteropoly decatungstothuliate (III) solutions revealed a bathochromic shift in  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  solution, which is caused by changes in the ligand environment (coordination polyhedron) of  $\text{Tm}^{3+}$  ion during the formation of Peacock-Weakley heteropoly anion in the solution.

3. Differential thermal analysis was carried out to study the process of thermal decomposition of the salt, while X-ray analysis revealed that the thermolysis of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  results in formation of  $\text{Na}_2\text{W}_2\text{O}_7$  and  $\text{Na}_{0.5}\text{Tm}_{0.5}\text{WO}_4$ .

4. Scanning electron microscopy confirmed the single-phasesness of the synthesized salt, and showed that the grain size of  $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2]\cdot 33\text{H}_2\text{O}$  is

within 200–350 nm.

#### Acknowledgements

The study was carried out within the Fundamental Research Programme funded by the Ministry of Education and Science of Ukraine (Project No. 0113U001530).

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Received 06.05.2015

#### THULIUM-CONTAINING HETEROPOLY TUNGSTATE WITH PEACOCK-WEAKLEY ANION: SYNTHESIS, PROPERTIES AND SURFACE MICROMORPHOLOGY

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The conditions for the synthesis of novel sodium heteropoly decatungstohalate (III)  $Na_4[Tm(W_5O_{18})_2] \cdot 33H_2O$  from an aqueous solution of sodium tungstate acidified to  $Z=0.80$  with a ratio  $n(Tm):n(W)=1:10$  and with acetone admixture were elaborated. By means of FTIR spectroscopy, we showed that the heteropoly anion contained in the isolated salt has a Peacock-Weakley structure. Thulium nitrate and sodium heteropoly decatungstohalate (III) solutions were analyzed using UV-Vis spectroscopy, and a bathochromic shift in the heteropoly salt solution was established that is caused by the change in coordination polyhedron of Tm (III) ion during transition from aqua complex to Peacock-Weakley heteropolyanion with coordination towards the heteroatom of lacunar pentatungstate anions in the form of square antiprisms. Using scanning electron microscopy, the morphology of heteropoly compound surface was studied; it was stated that the grain size is within the range of 200-350 nm. The single-phase condition of the synthesized salt was confirmed by the surface uniform contrast in backscattered electron mode. DTA method was used to study the thermal decomposition of the salt, while XRF analysis revealed the formation of sodium ditungstate and double sodium-thulium orthotungstate as a result of thermolysis.

**Keywords:** thulium; heteropoly tungstate; Peacock-Weakley structure; surface micromorphology.

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