

Y-, Sm-, and Er-Containing Heteropoly Tungstates With Peacock–Weakley Anion: Synthesis, Structure, and Surface Micromorphology

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Abstract – The conditions for the synthesis of novel sodium heteropoly decatungstometalates (III) – $\text{Na}_9\text{Y}(\text{W}_5\text{O}_{18})_2 \cdot 35\text{H}_2\text{O}$, $\text{Na}_{7.5}\text{H}_{1.5}[\text{Sm}(\text{W}_5\text{O}_{18})_2] \cdot 39.5\text{H}_2\text{O}$, $\text{Na}_9[\text{Er}(\text{W}_5\text{O}_{18})_2] \cdot 32\text{H}_2\text{O}$ from the aqueous solution of sodium tungstate acidified to $Z=0.80$ with a ratio $v(\text{X}):v(\text{W})=1:10$ and with acetone admixture were elaborated. Isolated salts were analyzed using Single Crystal X-ray Diffraction Analysis, FTIR and Raman spectroscopy, Scanning Electron Microscopy

Key words – Yttrium, lanthanides, polyoxotungstate, heteropoly anion, Peacock-Weakley structure, surface micromorphology.

I. 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 – lanthanides or 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 [1–2]. The second one includes 11th row compounds with Keggin-type lacunary metatungstate anion, $[\text{Ln}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{72}(\text{OH})_2]^{8-}$ [3].

As stated in [4], most of the currently known polyoxometalates are synthesized by self-assembly in solutions with mononuclear initial components.

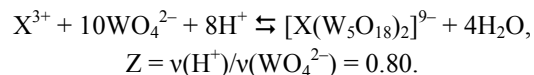
The present presents the results of synthesis of heteropoly compound with Peacock-Weakley type anion $\text{Na}_{9-m}\text{H}_m[\text{X}(\text{W}_5\text{O}_{18})_2] \cdot n\text{H}_2\text{O}$, which was carried out by the self-assembly from WO_4^{2-} and X^{3+} (X=Y, Sm, Er) in an acidified aqueous solution; it also studies its structures by Single Crystal X-ray Diffraction Analysis, FTIR and Raman spectroscopy, Scanning Electron Microscopy.

II. Experimental Part

In the study, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, HNO_3 , $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (all are ACS reagent grade) aqueous solutions were used.

The synthesis of $\text{Na}_{9-m}\text{H}_m[\text{X}(\text{W}_5\text{O}_{18})_2] \cdot n\text{H}_2\text{O}$ was carried out as following. Sodium tungstate solution was added to distilled water, and then HNO_3 solution was added dropwise with vigorous stirring. After that $\text{X}(\text{NO}_3)_3$

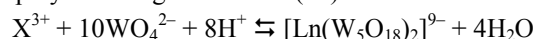
solution was added dropwise very slowly with vigorous stirring. It bears mentioning that each next drop of $\text{X}(\text{NO}_3)_3$ was added only after the disappearance of opalescence from the previous drop. The volume of the final aqueous solution amounted to 100 mL. Adding of reactants corresponds to the stoichiometry of the reaction, during which heteropoly decatungstometalate (III) anions are formed:



In order to isolate the resulting anion from the salt as a precipitate, 100 mL of acetone was added to the solution. Then, the resulting product was sealed and stored for 3 days at 6 °C that led to the formation of needle-like crystalline precipitate.

III. Results and their Discussion

Acidity $Z=0.80$ in the presence of stoichiometric amounts of reactive ions corresponds to the formation of heteropoly decatungstometalate (III) anions:



(X – Yttrium or lanthanides).

To isolate such particles with Y(III), Sm(III), and Er(III) ions-heteroatoms, sodium tungstate solutions ($C_w=0.1$ mol/L) acidified to $Z=0.80$ were used, to which $\text{X}(\text{NO}_3)_3$ solutions were added with vigorous stirring. After decanting of the components in a stoichiometric ratio of $\text{X}:\text{W}=1:10$, acetone was added to the system (up to 50 vol. %) and formation of needle-like crystalline precipitates were observed. Products yield were ~90 %; loss amounting to ~10 % were lost 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 EDX the isolated precipitates were assigned formulas $\text{Na}_9[\text{Y}(\text{W}_5\text{O}_{18})_2] \cdot 35\text{H}_2\text{O}$, $\text{Na}_{7.5}\text{H}_{1.5}[\text{Sm}(\text{W}_5\text{O}_{18})_2] \cdot 39.5\text{H}_2\text{O}$, $\text{Na}_9[\text{Er}(\text{W}_5\text{O}_{18})_2] \cdot 32\text{H}_2\text{O}$.

An X-ray diffraction study of single crystals of $\text{Na}_{7.5}\text{H}_{1.5}[\text{Sm}(\text{W}_5\text{O}_{18})_2] \cdot 39.5\text{H}_2\text{O}$ was carried out. The main crystallographic data are as follows: $M_r=3385.27$ g/mol, triclinic, $P-1$, $a=12.8938(4)$ Å, $b=13.1113(5)$ Å, $c=20.8847(7)$ Å, $\alpha=76.987(3)^\circ$, $\beta=84.049(3)^\circ$, $\gamma=77.415(3)^\circ$, $V=3351.8(2)$ Å³, $Z=2$, $T=100$ K, $\mu(\text{MoK}\alpha)=18.125$ mm⁻¹, $D_{\text{pozp}}=3.354$ g/cm³.

An X-ray diffraction study of single crystals of $\text{Na}_9[\text{Er}(\text{W}_5\text{O}_{18})_2] \cdot 32\text{H}_2\text{O}$ was carried out. Crystal The main crystallographic data are as follows: $M_r=3292.67$ g/mol, monoclinic, Cc , $a=11.4427(6)$ Å, $b=22.852(9)$ Å, $c=23.5459(2)$ Å, $\beta=91.813(1)^\circ$, $V=6154.1(7)$ Å³, $Z=4$, $T=100$ K, $\mu(\text{MoK}\alpha)=20.145$ mm⁻¹, $D_{\text{pozp}}=3.554$ g/cm³.

Nature of stretch and deformation vibrations in the tungsten-oxygen framework within FTIR and Raman spectra of air-dry samples of salts (Fig. 1–2) also indicates to the presence of Peacock-Weakley heteropoly anion of 10th row in them [5–6].

In this anion, two lacunar tetradentate pentatungstate-anions $\text{W}_5\text{O}_{18}^{6-}$ are coordinated to X-heteroatom, thus forming a coordination polyhedron in the shape of a square antiprism.

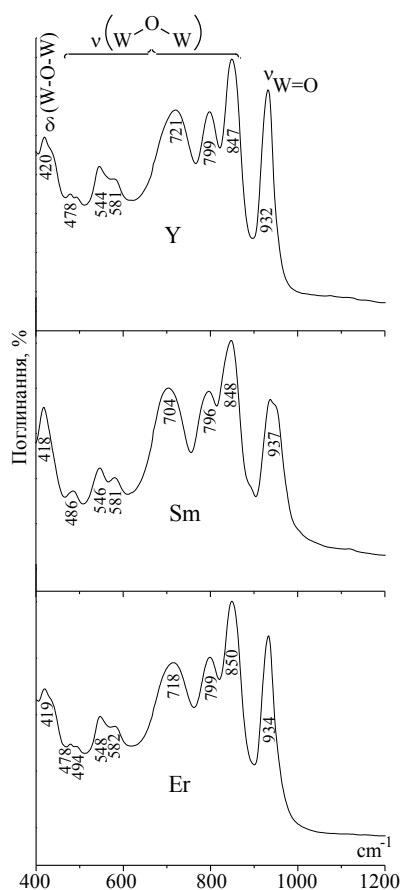


Fig. 1. FTIR spectra of crystalline salts with $[X(W_5O_{18})_2]^{9-}$ anion

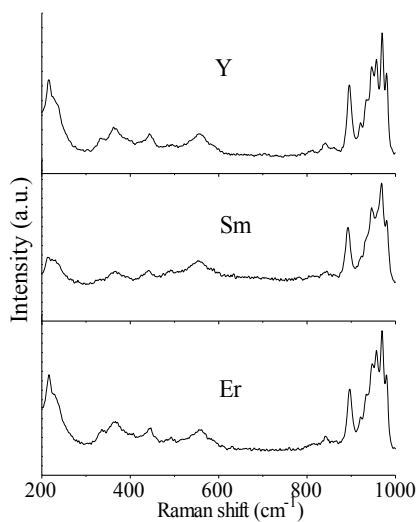


Fig. 2. Raman spectra of crystalline salts with $[X(W_5O_{18})_2]^{9-}$ anion

Microscopic analysis showed that the surface of grains in the isolated salts has fuzzy blurred edges. The size of the grains for the samples is within the range of 200–350 nm (Fig. 3).

Uniform surface contrast in backscattered electron (BEC) mode points to single-phasesness of the salts obtained.

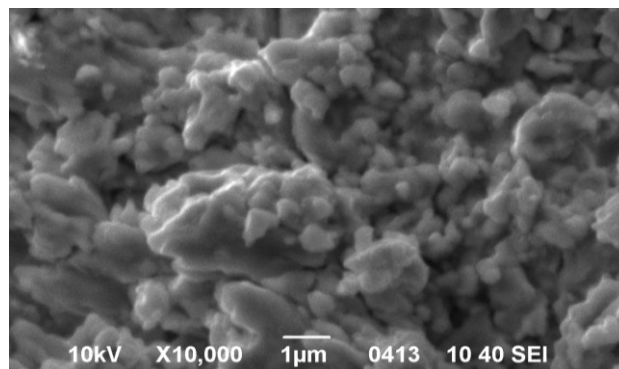


Fig. 3. SEM image of $Na_9[Y(W_5O_{18})_2] \cdot 35H_2O$ powder surface

On the micrographs of the salts powder in characteristic X-ray emission there are no regions with different surface morphology, and there is an even distribution of X, Na, W, O, without segregations and eliquations. These clearly indicate the formation of single-phase samples.

Conclusion

The conditions for the synthesis of a new heteropoly tungstates $Na_{9-m}H_m[X(W_5O_{18})_2] \cdot nH_2O$ ($X = Y$ ($m=0$; $n=35$), Sm ($m=1.5$; $n=39.5$), Er ($m=0$; $n=32$)) from the aqueous solution, acidified to $Z=v(H^+)/v(WO_4^{2-})=0.80$ with acetone adding, were determined. FTIR and Raman spectroscopy was used to show that the anion within the synthesized salt has a Peacock-Weakley structure.

Acknowledgements

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