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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis and Study of Sodium Vanadomanganate

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Abstract—Sodium 13-vanadomanganate $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$ (**I**) has been synthesized and studied by mass spectrometry, thermogravimetry, IR spectroscopy, and X-ray powder diffraction analysis. The crystals of compound **I** are monoclinic: a = 11.487 Å, b = 7.613 Å, c = 11.359 Å, β = 114.15°, V = 906.52 Å^3, ρ_{calcd} = 2.73 g/cm^3, Z = 1.

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Heteropoly compounds (HPCs) are intricate coordination compounds with a unique structure and diverse properties [1]. Different viewpoints about the structure and nature of HPCs have been rather completely covered in the literature [2–8]. The synthesis and physicochemical studies of new compounds and determination of trends in the behavior of their properties at different compositions and structures are significant for the development of HPC chemistry.

Interest in heteropolyvanadates is due to their practical use as catalysts in organic synthesis of bisphenols [9], which are stabilizers of polymers and oils [10].

The structures of heteropolyvanadates of manganese of different composition have been studied [11, 12], and the formation of the structure of these compounds depending on the synthesis conditions (pH, temperature).

This work is devoted to the synthesis and study of the physicochemical properties of sodium vanadomanganate $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$.

EXPERIMENTAL

Sodium vanadomanganate $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$ (**I**) was synthesized using a modified method [13]: a solution of manganese sulfate and sodium persulfate was added to a hot solution of sodium metavanadate acidified to pH 3 with nitric acid. The mixture was heated in a water bath until the volume was halved. The resulting solution was filtered and cooled in a desiccator, and after several days bright orange crystals of sodium vanadomanganate precipitated, which were filtered off and recrystallized from hot water.

The chemical composition of the synthesized compound was determined by mass spectrometry, and the content of water of crystallization was found by thermogravimetry. The elemental analysis data are given below.

For $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$ anal. calcd. (wt %): Na, 10.20; Mn, 3.48; V, 42.04; O, 38.55; H_2O, 5.70.

Found (wt %): Na, 10.05; Mn, 3.63; V, 43.06; O, 38.5; H_2O, 5.67.

Compound **I** was studied by X-ray powder diffraction analysis, IR spectroscopy, and thermogravimetry.

X-ray powder diffraction analysis was carried out on a Stoe IP automated diffractometer in the 2θ range 10°– 80°. The X-ray diffraction patterns were indexed using the Powder-2 program package.

The thermogravimetric study was carried out on a Paulik–Paulik–Erdey Q-1500 derivatograph in the temperature range 20–1000°C at a heating rate of 10 K/min for a weighed sample of 100 g. Calcined alumina served as the standard.

IR spectra of the compounds were recorded on a Perkin-Elmer spectrophotometer in the range 200–4000 cm^{-1}. Samples were prepared as potassium bromide pellets.

RESULTS AND DISCUSSION

As shown by the thermogravimetric study (Fig. 1), compound **I** has two endotherms. The first peak is observed at 120°C and corresponds to the removal of five molecules of water of crystallization, and the second endotherm at 500°C indicates the HPC decomposition. The scheme of thermal decomposition of compound **I** can be presented as follows:

$$Na_7[MnV_{13}O_{38}] \cdot 5H_2O \xrightarrow[-5H_2O]{120°C}$$

$$\longrightarrow Na_7[MnV_{13}O_{38}] \xrightarrow[-3/2\ O_2]{500°C}$$

$$\longrightarrow 4NaVO_3 + 3NaV_3O_8 + MnO_2.$$

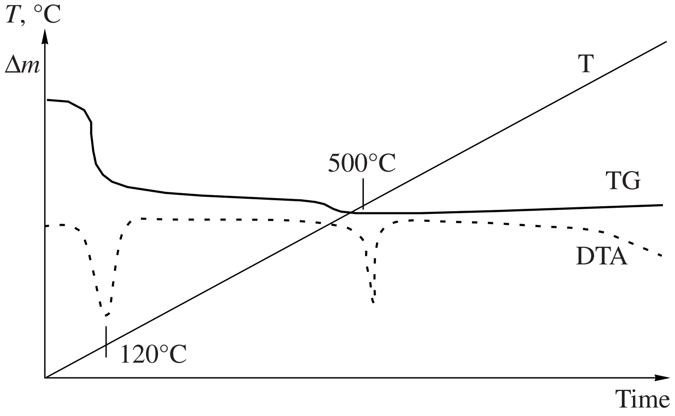

Fig. 1. Thermal analysis curves of $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$.

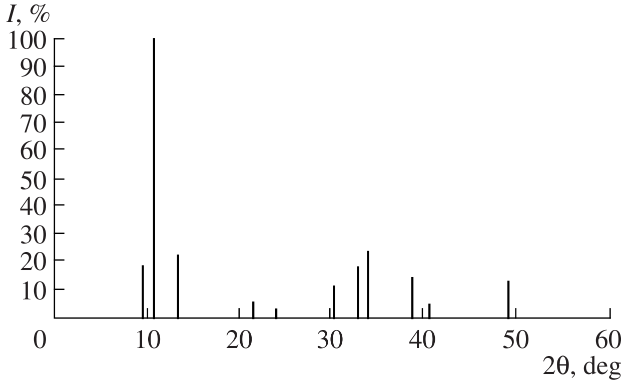

Fig. 2. Stick X-ray powder diffraction pattern of $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$.

X-ray powder diffraction analysis was carried out for both compound **I** and the products of its thermal decomposition in order to confirm the individual character and purity of the synthesized compound $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$, to obtain crystallographic data, and to analyze the thermal decomposition products. The X-ray diffraction patterns were indexed using the Powder-2 program package. The comparison of the obtained X-ray diffraction patterns with the PCPDFWIN database shows that compound **I** is free of possible admixtures and has monoclinic crystals with the unit cell parameters a = 11.487 Å, b = 7.613 Å, c = 11.359 Å, β = 114.15°, V = 906.52 Å^3. The pycnometric density of the compound found according to Syromyatnikov's method [14] is ρ_{exp} = 2.73 g/cm^3, and the number of formula units is Z = 1. The X-ray diffraction data are presented in Fig. 2 and Table 1.

Table 1. X-ray diffraction data for $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$

2θ, deg	d, Å	I, %	h	k	l
9.81	10.54	17.95	1	0	0
10.68	9.60	100	1	0	$\bar{1}$
13.45	7.63	21.98	0	1	0
21.48	4.79	5.31	2	0	$\bar{2}$
24.09	4.28	2.36	0	1	2
30.36	3.41	11.16	3	1	$\bar{1}$
31.38	3.30	2.10	3	1	$\bar{2}$
32.91	3.15	17.28	1	2	$\bar{2}$
33.79	3.07	22.94	2	2	0
38.76	2.69	13.54	3	2	$\bar{1}$
40.65	2.57	4.11	3	2	0
49.36	2.14	12.50	0	2	4

The X-ray diffraction patterns obtained at ambient temperature and after the thermal effect at 120°C are identical and correspond to the initial compound (Fig. 2), whereas those obtained at 500°C correspond to thermolysis products (Fig. 3, Table 2), confirming the proposed scheme of thermal decomposition of compound **I**.

Table 2. X-ray diffraction data for the thermal decomposition products

2θ, deg	d, Å	I, %	Compound	PCPDFWIN card number
12.47	7.10	11	$NaVO_3$	32–1198
13.34	6.63	100	NaV_3O_8	12–0676
20.90	4.46	20	NaV_3O_8	12–0676
21.85	4.06	6	NaV_3O_8	35–0436
24.62	3.61	60	$NaVO_3$	32–1197
29.58	3.017	10	$NaVO_3$	32–1198
30.94	2.88	44	NaV_3O_8	49–0997
31.38	2.84	14	$NaVO_3$	32–1197
32.08	2.78	41	$NaVO_3$	32–1197
33.41	2.68	35	$NaVO_3$	32–1197
34.49	2.59	20	NaV_3O_8	12–0676
36.88	2.43	49	MnO_2	44–0142
37.15	2.41	45	MnO_2	44–0992
39.22	2.29	8	$NaVO_3$	32–1197
46.07	1.96	20	NaV_3O_8	49–0997
47.70	1.90	13	MnO_2	44–0142
48.05	1.89	5	$NaVO_3$	32–1198
50.10	1.81	20	NaV_3O_8	12–0676

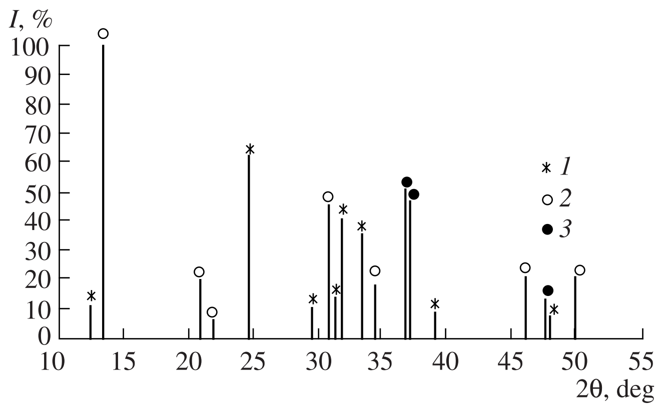

Fig. 3. Stick X-ray powder diffraction pattern of the thermal decomposition products of compound **I** at 500°C: (*1*) $NaVO_3$, (*2*) NaV_3O_8, and (*3*) MnO_2.

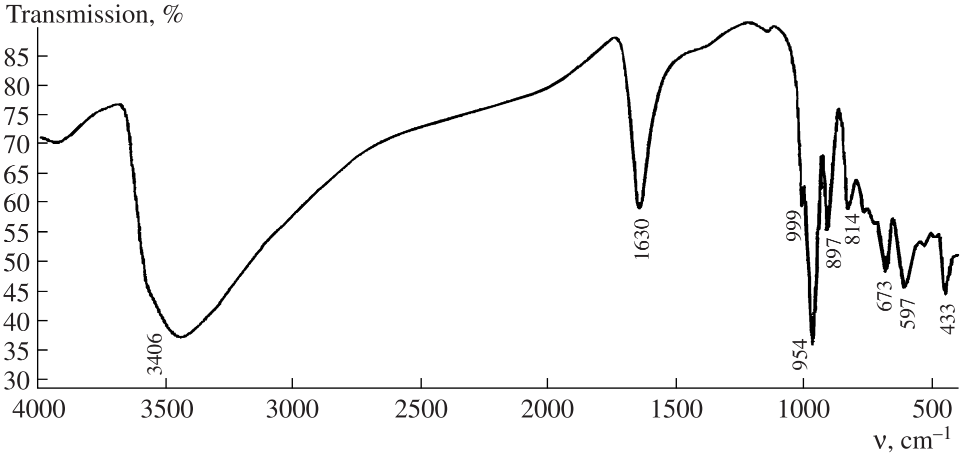

Fig. 4. IR spectrum of $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$.

The IR spectra of HPCs were studied in detail in [15]. The IR spectrum of compound **I** (Fig. 4) contains three groups of absorption bands at 400–1000 cm^{-1} attributed to vibrations of different metal–oxygen bonds of the complex heteropolyanion. According to published data [16], vibrations of the terminal (multiple) V=O bonds of the *cis*-VO_2 group in the heteropolyanion appear as a doublet at 900–1000 cm^{-1}. In our case, these are intense bands at 897 and 954 cm^{-1}. The bands at 450–600 cm^{-1} are assigned to vibrations of different types of the V–O–V bridging bonds. The broad intense band at 673 cm^{-1} and the band at 814 cm^{-1} are evidently due to vibrations of the Mn–O–V bridging bonds. In addition, the IR spectrum exhibits intense bands at 1630 and 3406 cm^{-1} assigned to vibrations of the hydroxy groups of the water molecules.

The identity of the IR spectrum of the $Na_7[MnV_{13}O_{38}] \cdot 5H_2O$ compound with the earlier studied HPC confirms our assumption about their resembling structures.

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