

# Thermal analysis of cesium zinc vanadates

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The thermal analysis of  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot 2.5\text{H}_2\text{O}$  and  $\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$  is described. The products of thermal treatment were investigated by X-ray phase analysis and infrared spectroscopy. It was found for cesium zinc metavanadate that some structural changes and partial reduction of vanadium(V) took place after dehydration. The reduction was also observed with cesium zinc decavanadate which decomposed at higher temperatures to give a mixture of cesium hexavanadate and zinc metavanadate.

Приводятся результаты термического анализа  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot 2.5\text{H}_2\text{O}$  и  $\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ . Продукты термической обработки были изучены при помощи рентгенофазового анализа и ИК спектроскопии. Было обнаружено, что в случае двойного метаванадата цинка и цезия наступают после дегидратации структурные превращения и частичное восстановление ванадия(V). Восстановление было обнаружено также в случае двойного декаванадата цинка и цезия, который при более высоких температурах разлагается с образованием смеси гексаванадата цезия и метаванадата цинка.

Thus far there is only little information on the temperature dependence of the physicochemical transformations of the hydrates of polyvanadates. Taking into account the structural features of the individual types of vanadates, it is evident that the extent of transformation must be different for individual types. In some cases only the structure changes may be assumed while in other cases the decomposition yielding different vanadates is to be expected at higher temperatures. In this respect, the most interesting results seem to be obtained by the study of meta- and decavanadates.

Up to now attention has been paid mostly to the structural aspects of the metavanadates of alkali metals and some bivalent metals. The characteristic feature of these compounds is the chain structure of the anion and a great variety of the coordination polyhedrons of vanadium. On the basis of this information as well as the results of the study of the thermal transformations of some metavanadates [1, 2] it is reasonable to assume that after the dehydration of the metavanadates of uni- and bivalent metals the structure of these substances may change to such an extent that the coordination number of vanadium changes while their polymer character remains preserved. The investigated cesium zinc metavanadate differs from other simple metavanadates by the presence of the large ions of cesium (0.169 nm) and the small ion of zinc (0.074 nm) in its structure, which may affect the thermal stability of this compound.

It ensues from some recent investigations that the thermal transformations of decavanadates are much greater than those of metavanadates [3—6]. These are the decomposition reactions in which the composition of products depends upon several factors. The investigation of cesium zinc decavanadate is a continuation of the study of potassium cadmium decavanadate [6]. Both the compounds belong to decavanadates of the general formula  $M_2^I M_2^{II} V_{10} O_{28} \cdot xH_2O$ .

## Experimental

$Cs_2Zn(VO_3)_4 \cdot 2.5H_2O$  and  $Cs_2Zn_2V_{10}O_{28} \cdot 14H_2O$  were prepared according to [7],  $Zn(VO_3)_2$  and  $Cs_2V_nO_{1n}$ , according to [8, 9].

The differential thermal analysis was performed on a derivatograph MOM (Budapest). Sensitivities: 1/10 in DTG, 100 in TG, 1/3 in DTA for  $Cs_2Zn(VO_3)_4 \cdot 2.5H_2O$  and 1/10 for  $Cs_2Zn_2V_{10}O_{28} \cdot 14H_2O$ , time 200 min, weighed amounts 300 mg for  $Cs_2Zn(VO_3)_4 \cdot 2.5H_2O$  and 120 mg for  $Cs_2Zn_2V_{10}O_{28} \cdot 14H_2O$ .

The isothermal heating of the compounds was performed in a crucible furnace alternatively in oxygen stream, *in vacuo*, over phosphorus pentoxide and sodium hydroxide. The samples were always heated to constant weight while the structural changes in substances were investigated simultaneously as a function of time.

The infrared spectra were taken on an instrument UR-20 (Zeiss, Jena) using the Nujol technique.

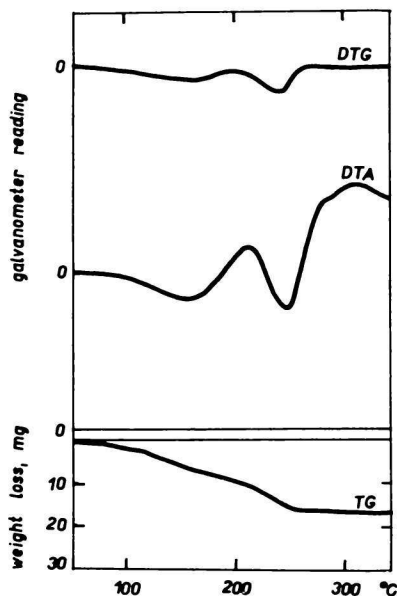
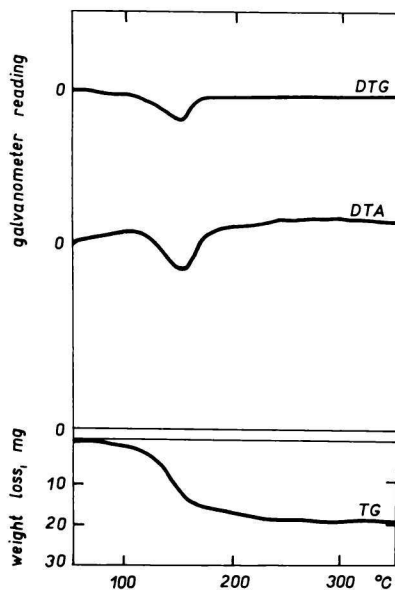
The X-ray diffraction patterns were taken on a diffractograph (Philips) equipped with a copper anticathode and a nickel filter.

The e.p.r. spectra were obtained on an instrument ER-9 (Zeiss, Jena) under equal conditions for both investigated compounds: HF(mod) = 35, NF(mod) = 50, height 10.55, width 70, NF(dB) = 8, HF(dB) = 0, ECHX = 29.625, frequency 9.37 GHz. Equal amounts of substance were used for all measurements.

## Results and discussion

The results of differential thermal analysis of  $Cs_2Zn(VO_3)_4 \cdot 2.5H_2O$  are shown in Fig. 1. The weight loss of 3.50% in the first stage (140°C) corresponds to the loss of 1.5 mole of water. The remaining mole of water is liberated in the second stage of dehydration (240°C). These endothermic processes are followed at 325°C by a vague exothermic maximum on the DTA curve and further course of the graph does not eliminate the possibility of other changes in the substance.

In the isothermal dehydration accomplished under the conditions stated in Table 1 cesium zinc metavanadate was obtained in the form of dihydrate, monohydrate, and anhydrous substance. The infrared spectra are presented in Table 2. It is obvious that the infrared spectra of all hydrates are equal. A similar consistency appears in the X-ray diffraction patterns, too (Table 3). This means that 1.5 mole of water is bound only by weak bonds in the lattice of the investigated metavanadate. However, this water is to be regarded as structural and not sorbed water. This is suggested by the desiccants used and the temperatures at which the

Fig. 1. Thermograms of  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot 2.5\text{H}_2\text{O}$ .Fig. 2. Thermograms of  $\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ .

lower hydrates discussed were obtained. A certain change in the infrared spectrum of the substance appears upon its full dehydration at 150°C, subsequently at 200°C, and at last at 280°C. Further temperature increase up to the melting of the substance at 390°C has practically no influence on its structure. On the basis of a comparison of individual infrared spectra obtained at increasing temperatures it may be assumed that no significant structural changes appear after the loss of crystal water. It is also obvious from Table 2 that the general character of the spectra of anhydrous cesium zinc metavanadate and cesium metavanadate is identical, which indicates an equal type of the V—O polyhedron in both salts. Therefore, similarly as in  $\text{CsVO}_3$  [10] a tetrahedral coordination of vanadium is assumed in this case, too.

Table 1

Products of isothermal dehydration of  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot 2.5\text{H}_2\text{O}$ 

Method of dehydration	Product	Weight loss, %	
		calculated	found
Vacuum, $\text{P}_2\text{O}_5$ , NaOH	$\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot 2\text{H}_2\text{O}$	1.17	1.16
From 50 to 100°C	$\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot \text{H}_2\text{O}$	3.57	3.59
From 150 to 390°C	$\text{Cs}_2\text{Zn}(\text{VO}_3)_4$	5.83	5.83

Table 2

Wavenumbers of crystal hydrates and anhydrous cesium zinc metavanadates

Assignment	$\text{Cs}_2\text{Zn}(\text{VO}_3)_x \cdot x\text{H}_2\text{O}$	$\text{Cs}_2\text{Zn}(\text{VO}_3)_4$ obtained at $t, ^\circ\text{C}$			$\text{CsVO}_3$
		150	200	280—390	
$\nu_{\text{as}}(\text{V—O}^*)$	455 vw				
	510 m	495 m 545 s	495 m 545 m 645 s	495 m 665 s	477 m 675 vs
	770 s	750—785 s			
$\nu_{\text{as}}(\text{V—O}^{**})$	830 vs	830 vs 895 s	827 vs 892 s	815 vs 890 s	857 s
	920 s				912 vs
	938 s	943 s	943 s	937 s 952 s	
	972 s	974 s	978 s	982 s	

\* Bridge oxygen atoms; \*\* terminal oxygen atoms.

vs — very strong, s — strong, m — medium, w — weak, vw — very weak;  $x = 1-2.5$ .

The conclusions on the structural transformations of the investigated metavanadate which were drawn from the changes in infrared spectrum were also confirmed by the analysis of the X-ray diffraction patterns (Table 3). It was also found that the dehydrated compound was not pure cesium zinc metavanadate because it contained an admixture of another substance the nature of which might be vanadium bronze. This conclusion follows from the fact that the dried samples contain somewhat less vanadium(V) than it would correspond to the pure compound of the composition  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$  (Table 4) as well as from the presence of vanadium(IV) which was detected by the e.p.r. method at  $g \sim 2$ .

Anhydrous cesium zinc metavanadate was also prepared by the reaction between zinc metavanadate and cesium metavanadate in the solid phase at temperatures 350—390°C (molar ratio 1 : 2). The compound thus prepared shows equal spectral and diffractive properties as the substance obtained by dehydration while the X-ray phase analysis confirms that a mixture of original metavanadates is not present. Thus it has been ascertained that a binary metavanadate containing cations with such different radii can also exist in the form of anhydrous salt. It is evident that owing to different bonding properties of the cations this salt is not very stable and melts already at a relatively low temperature (390°C). That manifests itself especially in comparison with the melting temperatures of pure zinc metavanadate (610°C) and cesium metavanadate (660°C). The change in the structure of anhydrous cesium zinc metavanadate which was observed in the temperature interval from 150 to 280°C may be related to the polarization properties of zinc which increase with temperature.

The results of differential thermal analysis of  $\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$  are presented in Fig. 2. The thermograms show that the dehydration of this compound is a one-step process in the temperature interval from 60 to 230°C. The weight loss is 15.96%.

By the isothermal drying of decavanadate at 220°C we can obtain an amorphous substance the infrared spectrum of which is considerably altered with respect to the spectrum of the starting hydrate (Table 5). A further temperature increase of about

Table 3

## Interplanar distances in nm

$\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot x\text{H}_2\text{O}$		$\text{Cs}_2\text{Zn}(\text{VO}_3)_4$ obtained at $t$ , °C					
		150		200		280—390	
$d_{hkl}$	$I_{\text{rel}}$	$d_{hkl}$	$I_{\text{rel}}$	$d_{hkl}$	$I_{\text{rel}}$	$d_{hkl}$	$I_{\text{rel}}$
0.606	14	0.612	13				
0.556	30	0.551	62	0.552	38	0.556	5
		0.534	10	0.532	5	0.530	5
						0.507	5
0.479	5	0.483	8	0.481	5	0.489	5
		0.458	6	0.458	5		
0.407	33	0.408	100	0.410	100	0.415	10
0.394	5	0.392	9	0.392	5	0.392	11
0.379	5	0.382	20	0.382	9	0.382	8
				0.373	5	0.374	9
0.351	20	0.351	45	0.351	40	0.355	38
		0.349	50	0.349	44		
		0.342	8	0.342	47	0.341	100
0.329	90	0.328	100	0.329	80	0.327	9
						0.324	9
		0.314	13	0.314	5	0.310	19
				0.305	13	0.306	15
0.303	10	0.304	35	0.303	10		
		0.297	18	0.296	7		
		0.292	5			0.283	15
				0.279	52	0.279	100
0.277	100	0.276	85	0.276	80		
		0.266	20	0.266	6		
0.264	10			0.264	5		
		0.261	11	0.261	5	0.260	18
0.251	7			0.249	5	0.250	18
0.248	19	0.247	23	0.246	9		
		0.245	10	0.245	5		
		0.239	26	0.240	8	0.236	5

Table 3 (Continued)

$\text{Cs}_2\text{Zn}(\text{VO}_3)_4 \cdot x\text{H}_2\text{O}$		$\text{Cs}_2\text{Zn}(\text{VO}_3)_4$ obtained at $t$ , °C							
		150		200		280—390			
$d_{hkl}$	$I_{\text{rel}}$	$d_{hkl}$	$I_{\text{rel}}$	$d_{hkl}$	$I_{\text{rel}}$	$d_{hkl}$	$I_{\text{rel}}$		
0.229	11	0.228	35	0.228	11	0.230	7		
						0.221	5		
						0.218	5		
				0.217	17	0.217	8	0.215	5
				0.238	5				
0.204	5	0.204	30	0.204	7				
		0.202	17	0.202	5				
0.196	32	0.198	8	0.197	6	0.197	14		
0.192	10	0.195	20	0.195	9				
		0.190	25	0.190	6	0.190	9		
						0.186	5		
				0.183	7	0.183	5		
				0.180	8	0.180	5	0.178	11
0.176	12	0.176	18	0.176	7				
		0.174	5	0.174	5				
		0.171	6	0.171	5	0.171	11		
		0.169	6						
0.168	14	0.167	8	0.167	5	0.166	5		
0.164	5	0.164	10	0.164	5				
0.163	5	0.160	7	0.161	5	0.162	8		
		0.159	8						
		0.158	8	0.158	5				
0.157	5	0.157	17	0.157	6				
				0.156	6				

80°C does not result in a more conspicuous change in the character of the substance. At 310°C this intermediate decomposes to give cesium hexavanadate, zinc metavanadate, and a small amount of other substance, most probably of vanadium bronze. This assumption is based on similar experimental findings as were those in the case of cesium zinc metavanadate (Table 6). The composition of this mixture is constant up to 400°C. At 410°C the mixture is subjected to a change, but it has not yet been possible to clear up the character of this change. By melting this intermediate at 470°C and cooling the melt rapidly a mixture of cesium hexavanadate and zinc metavanadate is obtained again. According to X-ray phase analysis (Table 7) this mixture is only little contaminated by an admixture of other substance. (Tetravalent vanadium is present in a lesser amount than at 310°C.)

In connection with the described thermal analysis of  $\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$  in

Table 4

Content of vanadium(V) in dried samples

Content of vanadium, %	Temperature of heating, °C		
	150	200	280—390
Calculated		28.03	
Found	26.46	26.50	27.30

Table 5

Wavenumbers of  $\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$  and of the products of thermal decomposition in  $\text{cm}^{-1}$ 

$\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$	Product obtained at $t$ , °C				$\text{Cs}_2\text{V}_6\text{O}_{16}$
	220	310	410	470	
415 w		405—425 s		405 w	405 w
465 w		470 s	435—485 vs	470 m	470 m
535 m	535—595 vs	528 vs		530—605 vs	521 vs
		545—565 vs	550 vs		588 m
600 m	635—670 s	600 s	605 s		625 w
			640—675 s		
755 m	770 s	740 vs	744 s	744 vs	744 vs
819 m		798 m	810 m		
848 s		847 m		850 m	
858 m	892 w	892 m			
		915 m	915 m		
960 vs	970 m	964 s	964 w	964 vs	964 vs
992 m		992 s	992 m		
		1010 w	1010 m	1010 m	1010 m

Table 6

Content of vanadium(V) in dried samples

Content of vanadium, %	Temperature of heating, °C			
	220	310	410	470
Calculated			37.62	
Found	36.03	36.10	37.00	37.08

Table 7

Interplanar distances in nm

Mixture		Cs <sub>2</sub> V <sub>6</sub> O <sub>16</sub> [19]		Zn(VO <sub>3</sub> ) <sub>2</sub> [8]	
$d_{hkl}$	$I_{rel}$	$d_{hkl}$	$I_{rel}$	$d_{hkl}$	$I_{rel}$
0.572	vw	0.575	vw		
0.495	vw	0.500	vw		
0.435	w			0.434	w
0.423	w	0.423	w		
0.409	s	0.407	s		
0.378	w				
0.368	vs	0.368	vs	0.364	m
0.333	m	0.332	m		
0.325	m	0.324	m		
0.308	vs	0.309	m	0.308	s
0.304	vs			0.303	vs
0.301	m	0.301	m		
0.295	m	0.295	m		
0.273	s	0.272	s	0.273	m
0.259	s	0.259	s		
0.248	w				
0.240	w			0.240	w
0.231	m			0.231	m
0.222	w			0.222	w
0.215	w			0.215	w
0.210	w			0.210	w
0.203	m			0.204	w
0.185	w			0.185	w
0.183	m	0.183	m		
0.176	w			0.176	w
0.164	w			0.164	w
0.163	w			0.163	w
0.155	w			0.155	w

which a partial reduction of vanadium(V) had been revealed, the correction of the mole number of crystal water in the molecular formula derived on the basis of chemical analysis was performed.

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