

## REINVESTIGATION OF PHASE EQUILIBRIA IN THE $V_2O_5$ –ZnO SYSTEM

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### Abstract

A diagram of phase equilibria established in a two-component oxide system  $V_2O_5$ –ZnO has been worked out applying differential thermal analysis and X-ray phase analysis as well as depending on investigations carried out with the aid of high-temperature X-ray attachment and scanning electron microscope linked to an X-ray microanalyser.

**Keywords:** DTA, phase equilibria, thermal properties,  $V_2O_5$ –ZnO, XRD

### Introduction

A two-component oxide system  $V_2O_5$ –ZnO has been the objective of studies conducted by many authors. The essential investigations were those concerning phase equilibria established in the title system [1–3]. However, the phase diagrams determined differ from each other. The authors are all agreed on the fact that the components of the system under consideration form three compounds:  $ZnV_2O_6$ ,  $Zn_2V_2O_7$ , and  $Zn_3(VO_4)_2$  [1–3]. On the other hand, Makarov *et al.* [3] and Clark and Pick [4] suggest that, apart from the three vanadates, there exists yet another compound,  $Zn_4V_2O_9$ , which melts incongruently at 910°C. Monocrystals of that phase, considered by the authors to be metastable, were obtained between a  $CO_2$ -laser generated flux and the solid ZnO/ $V_2O_5$  material [5].  $Zn_4V_2O_9$  crystallises in a monoclinic system, space group  $P2_1$  [5].  $ZnV_2O_6$  is the other compound not displaying polymorphism [6]. This vanadate crystallises in a monoclinic system, space group C2 [7], melts incongruently at 645°C, depositing a high-temperature  $\beta$ - $Zn_2V_2O_7$  modification [1].  $Zn_2V_2O_7$  occurs in two polymorphic forms, the temperature of the reversible process,  $\alpha$ - $Zn_2V_2O_7 \leftrightarrow \beta$ - $Zn_2V_2O_7$ , is 620°C according to [3], and 615°C – by [4]. The compound melts congruently at 890°C [3] or at 872°C [4].

There are wide divergences of the authors' opinion about polymorphism of zinc orthovanadate(V). Brown and Hummel [1], Pollard [2] and Hng and Knowles [8] point out that  $Zn_3(VO_4)_2$  occurs in three polymorphic forms, and the reversible process,  $\alpha$ - $Zn_3(VO_4)_2 \leftrightarrow \beta$ - $Zn_3(VO_4)_2$ , takes place at 795°C. The other reversible poly-

morphic process,  $\beta\text{-Zn}_3(\text{VO}_4)_2 \leftrightarrow \gamma\text{-Zn}_3(\text{VO}_4)_2$ , runs at 815°C. Clark and Pick [4] maintain that  $\text{Zn}_3(\text{VO}_4)_2$  exists in two polymorphic forms  $\alpha$  and  $\beta$ . A high-temperature  $\beta\text{-Zn}_3(\text{VO}_4)_2$  form breaks down at 815°C to yield  $\beta\text{-Zn}_2\text{V}_2\text{O}_7$  and  $\text{Zn}_4\text{V}_2\text{O}_9$  [4]. The thermal decomposition of zinc orthovanadate(V) was confirmed by Makarov *et al.* who suggest that the compound does not display polymorphism [3]. The structure of  $\text{Zn}_3(\text{VO}_4)_2$  is known, the compound crystallises in an orthorhombic system, space group Cmca [9].

In the light of the concisely demonstrated knowledge about the V<sub>2</sub>O<sub>5</sub>-ZnO system, we thought it advisable to verify the phase diagram of the system and to determine the thermal properties of some compounds occurring in it.

## Experimental

The following reactants were used in the experiments: V<sub>2</sub>O<sub>5</sub> (p.a., POCh, Gliwice, Poland), ZnO (p.a., Ubichem Ltd),  $\text{Zn}_2\text{V}_2\text{O}_7$  prepared according to [10] and  $\text{Zn}_3(\text{VO}_4)_2$  by applying the procedure of [11].

In order to determine the thermal properties of  $\text{Zn}_2\text{V}_2\text{O}_7$  and  $\text{Zn}_3(\text{VO}_4)_2$ , the experiments were carried out using a high-temperature X-ray attachment of an UVD-2000 type (Bourestnik, Sankt Petersburg, Russia) linked to an X-ray diffractometer of an HZG4/A2 type (Carl Zeiss, Jena, Germany).

Some selected samples were examined using scanning electron microscope (JSM-1600, Joel, Japan) linked to an X-ray microanalyser (ISIS 300, Oxford).

13 mixtures composed of the system's components, covering the whole component concentration range (Table 2) were prepared for the studies on phase equilibria established in the title system.

A detailed method of preparing samples, regarded as those being in an equilibrium state, was given in work [12].

The types of phases were established depending on powder diffraction patterns of the samples recorded by an X-ray diffractometer DRON-3 (Bourestnik, Sankt Petersburg, Russia), using  $\text{CoK}_\alpha$  radiation and a Fe filter. The identification of the phases was accomplished using the data of PDF charts [13] and those given in work [5].

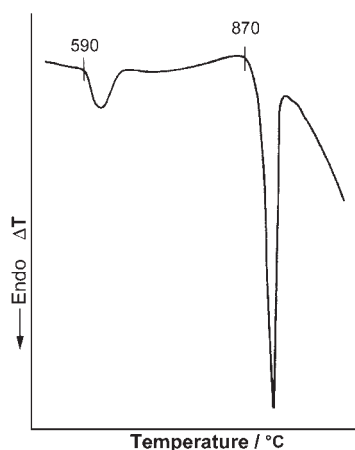
DTA method employed in measurements was aided by a MOM (Hungary) derivatograph in the temperature range of 20–1000°C. Samples of 1000 mg each, placed in quartz crucibles, were heated in air at a rate of 10 K min<sup>-1</sup>. The accuracy of reading thermal effect temperatures, i.e.  $\pm 5^\circ\text{C}$ , recorded on DTA curves was estimated by a repetition-test. Some chosen samples were examined by DTA method using an instrument of an SDT 2960 type (TA Instruments, USA). Samples of 5 mg each measured by DTA method in air, were placed in platinum crucibles and heated at a rate of 10 K min<sup>-1</sup>.

## Results and discussion

Verification of the phase equilibria diagram for the V<sub>2</sub>O<sub>5</sub>-ZnO system started from determining the thermal properties of Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Zn<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>. The investigations were carried out in a high-temperature X-ray attachment. Table 1 shows results obtained by XRD method for Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Zn<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> after each of the successive heating cycles. The data of Table 1 indicates that a reversible polymorphic process,  $\alpha$ -Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> ↔  $\beta$ -Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub>, takes place at ~590°C, that is, at a temperature lower than that given in works [3, 4]. An endothermic effect related with that polymorphic change was also recorded on the DTA curve of Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> (Fig. 1).

**Table 1** Heating conditions and X-ray phase analysis of samples of vanadates Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Zn<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> examined with the aid of high-temperature X-ray attachment

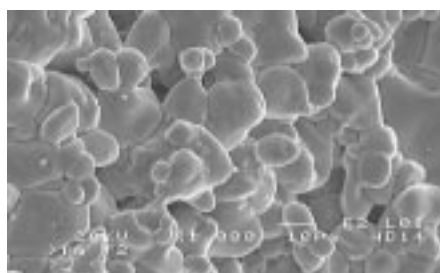
Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>			Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>		
Temp./°C	Time/h	Phases detected	Temp./°C	Time/h	Phases detected
580	0.5	$\alpha$ -Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	750	1.0	Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>
590	0.5	$\beta$ -Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	780	1.0	Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>
			790	1.0	Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub> , $\beta$ -Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub> , Zn <sub>4</sub> V <sub>2</sub> O <sub>9</sub>
			790	2.0	$\beta$ -Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub> , Zn <sub>4</sub> V <sub>2</sub> O <sub>9</sub> , Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>
			800	1.0	$\beta$ -Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub> , Zn <sub>4</sub> V <sub>2</sub> O <sub>9</sub>



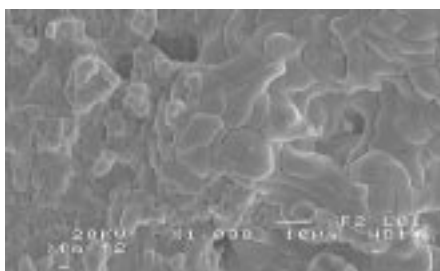
**Fig. 1** DTA curve of Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub>

The data of Table 1 also show that heating of Zn<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> up to 780°C did not affect the X-ray diffraction pattern of the phase at any rate. It was only when it was heated at 790°C for 1 h that negligible amount of  $\beta$ -Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Zn<sub>4</sub>V<sub>2</sub>O<sub>9</sub> were de-

tected beside  $Zn_3(VO_4)_2$ . Further heating at this temperature gave rise to increase in the content of  $\beta$ - $Zn_2V_2O_7$  and  $Zn_4V_2O_9$ , and consequential decrease in the content of original  $Zn_3(VO_4)_2$ . The sample heated at  $800^\circ\text{C}$  for 1 h did not contain  $Zn_3(VO_4)_2$  but products of its decomposition, i.e.  $\beta$ - $Zn_2V_2O_7$  and  $Zn_4V_2O_9$ . Figure 2 shows a SEM image of the compound  $Zn_3(VO_4)_2$  heated at  $750^\circ\text{C}$  for 3 h to be quenched to ambient temperature afterwards. Figure 3 shows a SEM image of the same sample taken after keeping it in a thermostat at  $820^\circ\text{C}$  for 3 h and quenched, too. No areas of amorphous forms have been noticed in the pictures. A sample of  $Zn_3(VO_4)_2$  heated at  $750^\circ\text{C}$  and then analysed by an X-ray microanalyser contained only such crystals that were corresponding to the  $Zn_3(VO_4)_2$ . The same sample heated at  $820^\circ\text{C}$  comprised two types of crystals, which were attributed to  $Zn_2V_2O_7$  and  $Zn_4V_2O_9$ .



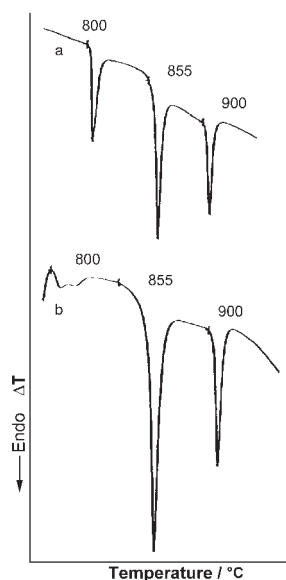
**Fig. 2** SEM image of  $Zn_3(VO_4)_2$  heated at  $750^\circ\text{C}$  during 3 h



**Fig. 3** SEM image of  $Zn_3(VO_4)_2$  heated at  $820^\circ\text{C}$  during 3 h

Both the results of investigations carried out in high-temperature X-ray attachment and investigations conducted by scanning electron microscope suggest that  $Zn_3(VO_4)_2$  do not display polymorphism but at  $800^\circ\text{C}$  in the solid state it breaks down into two solid phases,  $\beta$ - $Zn_2V_2O_7$  and  $Zn_4V_2O_9$ . Figure 4a presents a DTA curve of  $Zn_3(VO_4)_2$ , and by comparison Fig. 4b shows a DTA curve of an equimolar  $Zn_2V_2O_7/Zn_4V_2O_9$  mixture. The first endothermic effect recorded on the DTA curve of  $Zn_3(VO_4)_2$ , starting at  $800\pm 5^\circ\text{C}$ , is deemed to be related with thermal decomposition of the phase. The second of the endothermic effects is involved in melting of products of  $Zn_3(VO_4)_2$  thermal decomposition, and the last effect is developed by melting  $Zn_4V_2O_9$ . On the DTA curve of the equimolar  $Zn_2V_2O_7/Zn_4V_2O_9$  mixture, apart from effects bound with melting of the mixture, there was noticed a small endothermic effect at  $800\pm 5^\circ\text{C}$ . The presence of this effect implies that heating in the DTA

apparatus must have given rise to a reaction between Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Zn<sub>4</sub>V<sub>2</sub>O<sub>9</sub>, to yield Zn<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> in negligible amounts, that decomposes at 800±5°C to the initial mixture.



**Fig. 4** DTA curves of a – Zn<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> and b – equimolar mixture of Zn<sub>4</sub>V<sub>2</sub>O<sub>9</sub> with Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub>

Table 2 shows compositions of initial mixtures, heating conditions and XRD data for samples in a state of equilibrium. It follows from the content of Table 2 that four compounds exist in the investigated system, one of them being identified only in samples heated at 740–900°C.

**Table 2** Contents of initial mixtures, heating conditions and X-ray phase analysis of samples in an equilibrium state

Contents of initial mixtures/ V <sub>2</sub> O <sub>5</sub> mol%	Heating conditions	Contents of equilibrium samples
10.00; 15.00; 20.00	500°C [24 h]+520°C [24 h] +700°C [24 h×2]	Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub> , ZnO
10.00; 15.00 20.00	+760°C [24 h×2]	Zn <sub>4</sub> V <sub>2</sub> O <sub>9</sub> , ZnO Zn <sub>4</sub> V <sub>4</sub> O <sub>9</sub>
25.00		Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>
27.50; 30.00	520°C [24 h×2]	α-Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub> , Zn <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>
33.33	+550°C [24 h×2]	α-Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
40.00	+600°C [24 h]	ZnV <sub>2</sub> O <sub>6</sub> , α-Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
50.00		ZnV <sub>2</sub> O <sub>6</sub>
60.00; 70.00	500°C [24 h] +520°C [24 h] +550°C [24 h×2]	V <sub>2</sub> O <sub>5</sub> , ZnV <sub>2</sub> O <sub>6</sub>
80.00; 90.00	500°C [24 h] +520°C [24 h]	V <sub>2</sub> O <sub>5</sub> , ZnV <sub>2</sub> O <sub>6</sub>



- it is proved that Zn<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> does not display polymorphism, but at 800°C it breaks down in a solid phase to yield β-Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Zn<sub>4</sub>V<sub>2</sub>O<sub>9</sub>,
- a verified diagram of phase equilibria established in the V<sub>2</sub>O<sub>5</sub>-ZnO system is worked out.

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