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REINVESTIGATION OF SYSTEM CdO–V_2O_5 IN THE SOLID STATE

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As a result of solid-state reactions three cadmium vanadates(V) have been obtained, i.e. CdV_2O_6, $Cd_2V_2O_7$ and $Cd_4V_2O_9$. Melting temperature and the product of melting has been determined for $Cd_4V_2O_9$. Thermal properties of the obtained cadmium vanadates(V) have been reinvestigated. The phase equilibria being established in the CdO–V_2O_5 system over the whole components concentration range up to the solidus line were described.

Keywords: *cadmium oxide, cadmium vanadates, DTA, solid-state reactions, XRD*

Introduction

Following the review of literature it can be assumed that the CdO–V_2O_5 system has been subject of studies conducted by many authors for a number of years [1–12] and yet there are still significant divergences concerning both the kind of the phases formed in this system, as well as their thermal properties. Hence three versions of the phase equilibrium diagram of this system are known [1–3].

Angenault [1] described three cadmium vanadates(V), namely: CdV_2O_6, $Cd_2V_2O_7$ and $Cd_4V_2O_9$. According to Brown [2], cadmium orthovanadate(V), i.e. $Cd_3V_2O_8$, exists apart from cadmium meta- and divanadate(V). The author claims that $Cd_4V_2O_9$, described by Angenault, does not exist but is a mixture of $Cd_3V_2O_8$ and CdO. In much later work, Nord *et al.* [4] report on obtaining $Cd_3V_2O_8$, whose X-ray characteristics is compatible with that provided by Brown [2]. At the same time Fotiev *et al.* [3] does not deny the existence of $Cd_3V_2O_8$, although the attempts to obtain this phase proved unsuccessful. The author assumes that this compound, similarly to $Zn_3V_2O_8$, might decompose in the solid state in the range of 800–840°C temperatures. They are of the opinion that if the formation of CdV_2O_6 and $Cd_2V_2O_7$ raises no doubts, then the existence of $Cd_3V_2O_8$ and $Cd_4V_2O_9$ is still unclear [3, 5]. The synthesis of $Cd_4V_2O_9$ was also performed by Tsuzuki *et al.* [6]. No more works devoted to the characteristics of both $Cd_3V_2O_8$ and $Cd_4V_2O_9$ have been found. According to Angenault [1] $Cd_4V_2O_9$ melts incongruently at the temperature of 952°C.

Cadmium divanadate(V) and metavanadate(V) were, however, subject of numerous studies. $Cd_2V_2O_7$ does not exhibit polymorphism and melts congruently at the temperature, which according to different authors is 978°C [1], 1000°C [2], 1020°C [3]. Cadmium metavanadate(V) crystallizes in two polymorphous forms [1–3, 7–12]. One of them was designated as α- or P-; the other one as β- or B-. P-CdV_2O_6 has the structure of the pseudo-brannerite type, whereas B-CdV_2O_6 demonstrates the brannerite type structure. The authors of the works [1–3, 7–9, 12] believe that P-CdV_2O_6 is the low-temperature form and consider B-CdV_2O_6 as the high-temperature one. It was proved in works [10, 11] that B-CdV_2O_6 is the low-temperature form, whereas P-CdV_2O_6 the high-temperature one. According to the authors [3, 7] the temperature of the polymorphous conversion of the low-temperature form to the high-temperature one is about 700°C, and yet works [2, 11] reported that the conversion takes place at the temperature 180 or 170°C [8, 10]. Tsuzuki *et al.* [11] claims that the high-temperature form is meta-stable and after being cooled down to room temperature it can remain in it. The high-temperature form conversion to the low-temperature one requires its freezing in liquid nitrogen or grinding. Mocała and Ziółkowski [10] are of the opinion that by cooling the high-temperature form to room temperature one obtains the low-temperature modification. Thus the thermal characteristics of cadmium metavanadate(V) are not unambiguously determined. The only fact, though reported on by different authors, that is the temperature of the incongruent melting of CdV_2O_6 does not differ, comprising 800°C [1–3, 10].

The purpose of this work was to check which phases are formed in the CdO–V_2O_5 system, the verification of their thermal properties as well as the

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working out the phase diagram of the investigated system up to the solidus line.

Experimental

27 mixtures of $CdCO_3$ (p.a., Serva, Germany) and V_2O_5 (p.a., Riedel-de Haën, Germany) were prepared for the investigations. The reacting substances were weighed in appropriate portions, homogenized by grinding, shaped into pellets and heated in several stages in the atmosphere of air until the state of equilibrium was obtained. After each heating stage the samples were gradually cooled down in the furnace to room temperature and, after grinding, they were examined by the XRD method, some selected samples also by the DTA one.

The types of phases were established depending on powder diffraction patterns of the samples [13–18] obtained using the X-ray diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia) and Ni-filtered Cu radiation. Additional experiments were carried out using a high-temperature X-ray attachment of a UVD-2000 type (Bourevestnik, Sankt Petersburg, Russia) linked to an X-ray diffractometer of an HZG4/A2 type (Carl Zeiss, Jena, Germany). The identification of the phases was conducted on the basis of XRD characteristics contained in the PDF cards [19].

The DTA/TG measurements with the use of a Paulik–Paulik–Erdey derivatograph (MOM, Hungary) were performed in corundum crucibles in the temperature range 20–1020°C. Samples of 500 mg each were heated in air at a rate of 10°C min^{-1}.

Some selected samples were examined using scanning electron microscope (JSM-1600, Jeol, Japan).

Results and discussion

Table 1 presents the compositions of the samples prepared for the tests, the conditions of the preparation and the phases detected in particular samples after the last stage of calcination. From the data included in Table 1 it follows that three cadmium vanadates(V), that is: CdV_2O_6, $Cd_2V_2O_7$ and $Cd_4V_2O_9$ are formed as a result of a reaction taking place in the solid phase. Cadmium orthovanadate(V) has not been obtained, though.

Additional attempts to receive $Cd_3V_2O_8$ were conducted. Sample 7 (Table 1), corresponding with its composition to $Cd_3V_2O_8$ was heated at 800°C for 12 h, and then it was rapidly cooled down. On the diffraction pattern of this sample was recorded a set of lines further characterizing two compounds: $Cd_4V_2O_9$ and $Cd_2V_2O_7$. Next, sample 7 was placed in the high-temperature X-ray attachment, heated up to 800°C and temperated at constant temperature for 4 h. The XRD analysis results taken after each hour of thermostating indicate that the composition of the tested sample did not undergo any changes. Both experiments were repeated at the temperature of 750°C following the suggestions of the authors [3] regarding the decomposition of $Cd_3V_2O_8$ in the range of temperature from 800 to 840°C. The obtained results did not differ from these at 800°C. None of the three ways employed was successful with regard to obtaining the $Cd_3V_2O_8$ compound. The mentioned ways were as follows: the conventional method of long-lasting heating, using the high-temperature X-ray attachment as well as heating and rapid cooling down. The sample which corresponded with its composition to that of $Cd_3V_2O_8$ (the compound characterized by the melting temperature of 1000°C and described by the authors [2, 4]) is a mixture of $Cd_2V_2O_7$ and $Cd_4V_2O_9$ melting at the temperature of 840±5°C.

The purpose of further studies was the verification of the thermal properties of the obtained cadmium vanadates(V). $Cd_4V_2O_9$ was subjected to the tests as the first. Two endothermic effects: the first with its onset temperature equal to 875±5°C and the second with its onset temperature equal to 980±5°C were recorded on the DTA curve of $Cd_4V_2O_9$ (Fig. 1a). In order to determine the type of the process relating to the first effect, the $Cd_4V_2O_9$ sample was heated at 880°C for 2 h, and next cooled down rapidly to room temperature. At the moment of removing the

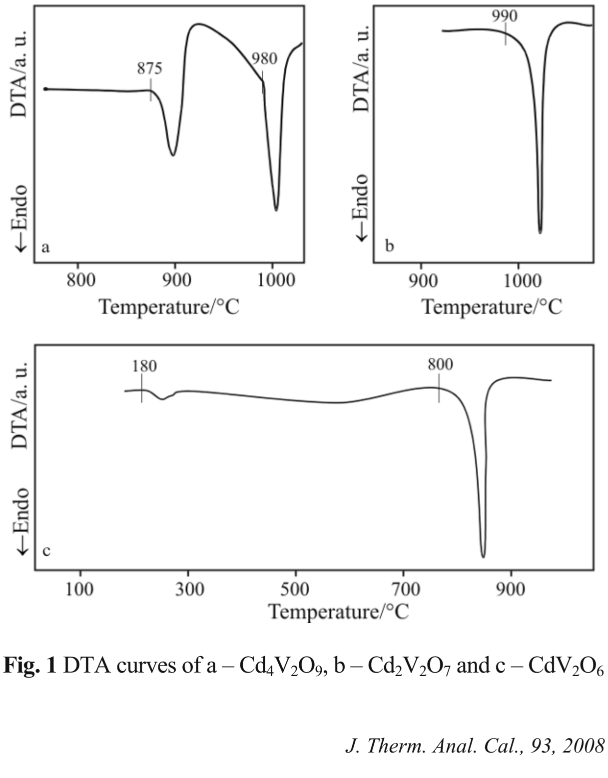

Fig. 1 DTA curves of a – $Cd_4V_2O_9$, b – $Cd_2V_2O_7$ and c – CdV_2O_6

Table 1 The composition of initial mixtures, conditions of preparation (heating temperature and time) and the XRD results for all samples

No.	Contents of initial mixtures/mol%		Heating conditions	Contents of equilibrium samples
	CdO	V_2O_5		
1	95.00	5.00	550°C (12 h)+600°C (12 h)+650°C (12 h)+700°C (12 h)+750°C (12 h)+780°C (12 h)+840°C (2·12 h)	$Cd_4V_2O_9$, CdO
2	90.00	10.00		
3	87.50	12.50		
4	85.00	15.00		
5	80.00	20.00	550°C (12 h)+600°C (12 h)+650°C (12 h)+700°C (12 h)+750°C (12 h)+800°C (2·12 h)	$Cd_4V_2O_9$
6	77.50	22.50		$Cd_4V_2O_9$, $Cd_2V_2O_7$
7	75.00	25.00		
8	72.50	27.50		
9	70.00	30.00		
10	66.70	33.30		$Cd_2V_2O_7$
11	62.50	37.50	550°C (12 h)+600°C (12 h)+650°C (12 h)+700°C (12 h)+750°C (12 h) (2·12 h)	$Cd_2V_2O_7$, B-CdV_2O_6
12	60.00	40.00		
13	67.50	42.50		
14	55.00	45.00		
15	50.00	50.00	550°C (12 h)+580°C (4·12 h)	B-CdV_2O_6
16	45.00	55.00		B-CdV_2O_6, V_2O_5
17	42.50	57.50		
18	40.00	60.00		
19	35.00	65.00		
20	30.00	70.00		
21	25.00	75.00		
22	20.00	80.00		
23	17.50	82.50		
24	15.00	85.00		
25	12.50	87.50		
26	10.00	90.00		
27	5.00	95.00		

sample from the furnace at the temperature of 880°C, it was melted. After being cooled down the sample adopted the glassy form and its diffraction pattern did not reveal the clearly formed reflexes. The process of $Cd_4V_2O_9$ melting was repeated, and after the 2 h heating at 880°C was completed, the sample was cooled down to room temperature during 0.5 h. The obtained product did not have the glassy form any longer, and on its diffraction pattern were recorded the lines characterized by high intensity typical of $Cd_2V_2O_7$. The received results indicate that $Cd_4V_2O_9$ melts at the temperature of 875±5°C, and $Cd_2V_2O_7$ is most likely to be the solid product of the process. The melting temperature determined by us is thus noticeably, lower than that suggested by Angenault [1]. Figure 2 presents a SEM image of $Cd_4V_2O_9$, where as Fig. 3 shows a SEM image of the same sample heated for 2 h at 880°C and cooled down during 0.5 h. The second endothermic effect recorded in the DTA curve of $Cd_4V_2O_9$, with the onset temperature 980±5°C, is believed to be due to the melting of $Cd_2V_2O_7$ (the solid product of the melting $Cd_4V_2O_9$).

In the course of the next activities the temperature of $Cd_2V_2O_7$ melting was checked since this temperature, when provided by different authors [1–3] fluctuates within the following range, namely 978–1020°C. On the cadmium divanadate(V) DTA curve (Fig. 1b) was recorded only one endothermic effect with its onset temperature equal to 990±5°C. The results of the XRD analysis of the $Cd_2V_2O_7$ compound, heated at 1050°C for 2 h, and next cooled down rapidly to ambient temperature, confirm that the

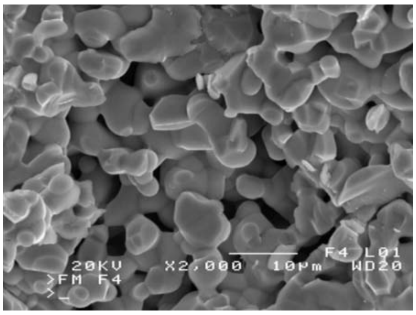

Fig. 2 SEM image of $Cd_4V_2O_9$

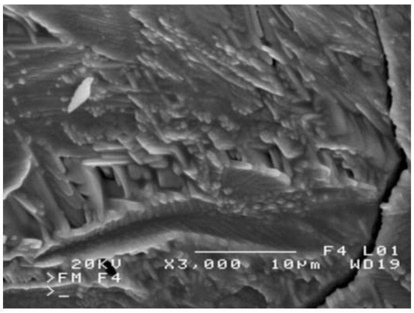

Fig. 3 SEM image of $Cd_4V_2O_9$ heated at 880°C during 3 h

recorded endothermic effect is connected with the congruent melting of $Cd_2V_2O_7$.

The DTA curve of cadmium metavanadate(V) (Fig. 1c) reveals two endothermic effects. The first effect, the smaller with its onset temperature equal to 180±5°C, the other one to 800±5°C. With the view to determining the process connected with the first endothermic effect, B-CdV_2O_6 (sample 15) was heated at 250°C for 3 h, and next cooled down rapidly and subjected to the XRD analysis, without grinding. The diffraction pattern demonstrated that next to the lines characterizing the B-CdV_2O_6 form, the lines typical of P-CdV_2O_6, were recorded. The diffraction pattern of the sample heated at the temperature of 250°C for 3 h, rapidly cooled down and ground, showed only the B-CdV_2O_6 lines. Hence it was found that the endothermic with the onset temperature equal to 180±5°C, is linked with the polymorphic transition of the low-temperature B-CdV_2O_6 form to the high-temperature one, that is P-CdV_2O_6, which confirms the data presented in works [10, 11], however contradicts the information found in works [2, 3, 7–9, 12]. Moreover, the conducted experiment indicates that the high-temperature cadmium metavanadate(V) form can (at least partially) exist at room temperature, and the grinding facilitates its conversion to the low-temperature form, which is in agreement with Tsuzuki's findings [11]. The additional experiments were carried out in a high-temperature X-ray attachment. A sample of B-CdV_2O_6 was heated to given temperatures which were stabilized for 0.5 h. This experiment have proved that the polymorphic transition of B-CdV_2O_6 to P-CdV_2O_6 starts at 160 and 180°C is completed. Further heating of P-CdV_2O_6 up to 730°C and thermostating at this temperature for 4 h did not bring about any transformation.

Cadmium metavanadate(V) was also subjected to heating for 3 h, above the temperature of the beginning of the second endothermic effect, i.e. at 820°C, and next cooled down rapidly. On the diffraction pattern of the obtained sample were recorded the lines characterizing $Cd_2V_2O_7$. Thus, the second endothermic effect, recorded on the DTA curve of CdV_2O_6 is related to the incongruent melting of this compound.

Figure 4 presents a phase diagram of the $CdO–V_2O_5$ system built on the basis of the DTA curves and the results of the XRD analysis of the samples at equilibrium belonging to the studied system (Table 1). The temperatures of the solidus line were determined on the basis of the onset temperatures of the first endothermic effects, being not due to polymorphic transition recorded on the DTA curves of the examined samples.

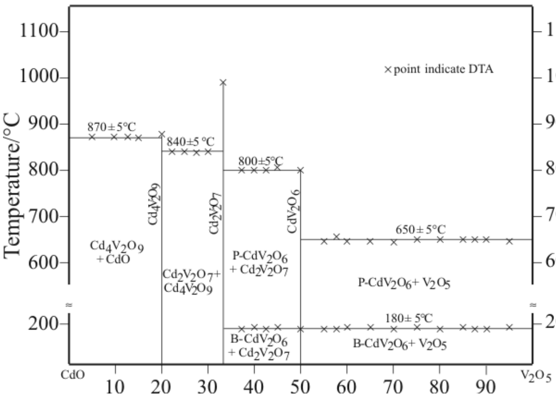

Fig. 4 Phase diagram of $CdO–V_2O_5$ system up to the solidus line

Conclusions

The results of the follow-up studies:

- Three cadmium vanadates: CdV_2O_6, $Cd_2V_2O_7$ and $Cd_4V_2O_9$ are formed in the $CdO–V_2O_5$ system according to the authors [1, 6]. Suggestions of Fotiev *et al.* [3] about decomposition of '$Cd_3V_2O_8$' was not confirmed. The compound '$Cd_3V_2O_8$' described by the authors [2, 4] is the mixture of $Cd_2V_2O_7$ and $Cd_4V_2O_9$.
- The polymorphous conversion of cadmium metavanadate(V) starts at 160±5 and 180±5°C is completed. B-CdV_2O_6 is the low-temperature form, P-CdV_2O_6 is the high-temperature form. It confirms information given by authors [10, 11], but it

contradicts the data presented in works [2, 3, 7–9, 12].

- $Cd_2V_2O_7$ melts at the temperature of 990±5°C.
- $Cd_4V_2O_9$ melts incongruently at the temperature of 875±5°C, depositing solid $Cd_2V_2O_7$. This temperature is 77°C lower than that determined by Angenault [1].

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