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NEW PHASE IN THE SYSTEM $FeVO_4$–$Cd_4V_2O_9$

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A new phase $Cd_4Fe_{7+x}V_{9+x}O_{37+4x}$, where $-0.5<x<1.5$, has been obtained in the solid-state in the $FeVO_4$–$Cd_4V_2O_9$ system. The temperature of incongruent melting and the unit cell volume of this phase decrease with decreasing the content of cadmium. The IR spectrum and SEM image of the new phase are presented.

Keywords: *CdO–V_2O_5–Fe_2O_3 system, DTA, howardevansite type structure, IR, XRD*

Introduction

Following the studies on the reactivity of iron(III) orthovanadate(V) towards di- and orthovanadates(V) of divalent metals a number of new phases, not described earlier, have been obtained. The compounds belonging to the $M_2FeV_3O_{11}$ (M=Zn, Co, Mg) family are the products of a reaction of $FeVO_4$ with $M_2V_2O_7$ [1–4]. The phases of the howardevansite type structure $M_3Fe_4V_6O_{24}$ (M=Zn, Mg) [5, 6] and $Co_{2.616}Fe_{4.256}V_6O_{24}$ [7] are formed as a result of heating the mixtures of $FeVO_4$ with $M_3V_2O_8$.

It follows from the literature review that the reactivity of $FeVO_4$ towards cadmium vanadates(V) has not been subjected of investigation so far. Also there is no information on the compounds formed with all the components of the CdO–V_2O_5–Fe_2O_3 system being involved. Hence it was interesting to check whether the phases belonging to the phase families produced in similar MO–V_2O_5–Fe_2O_3 (M=Zn, Co, Mg) systems, are formed in this one.

In this work the physicochemical properties of a new, not yet described phase, formed in the $FeVO_4$–$Cd_4V_2O_9$ system, are presented.

Experimental

The following reactants were used in the experiments: $CdCO_3$ (p.a., Serva, Germany), V_2O_5 (p.a., Riedel-de Haën, Germany), α-Fe_2O_3 (p.a., POCh, Poland), $FeVO_4$, $Cd_2V_2O_7$ and $Cd_4V_2O_9$. The vanadates were obtained as a result of heating stoichiometric mixtures of Fe_2O_3 with V_2O_5 or $CdCO_3$ with V_2O_5 in the following stages:

- synthesis of $FeVO_4$: 560°C (20 h)+590°C (20 h·2)
- synthesis of $Cd_2V_2O_7$: 600°C (20 h·2)+ 750°C (20 h)+790°C (20 h)
- synthesis of $Cd_4V_2O_9$: 600°C (20 h)+ 790°C (20 h·2)

The reactions were carried out by conventional method of calcining samples [8–12]. The reacting substances were homogenized by grinding and heated for several stages under air. On completion of each heating stage the samples were gradually cooled in furnace to ambient temperature, ground and examined by XRD method, some selected samples also by DTA. The process of heating the sample was finished when its composition did not undergo any changes after the next two heating stages.

The DTA measurements were performed by means of the derivatograph Paulik–Paulik–Erdey (MOM, Hungary), in the atmosphere of air, in the temperature range 20–1000°C. Samples of 500 mg were heated in quartz crucibles at a rate of 10°C min^{-1}.

The kind of phases occurring in the samples was determined on the ground of their powder diffraction patterns [13–15], obtained using the X-ray diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia) and Ni-filtered Cu radiation. The identification of the phases was conducted with the aid of XRD characteristics given in PDF cards [16]. The powder diffraction patterns were indexed by means of the Refinement program of DHN/PDS package, using α-Al_2O_3 as the internal standard.

The IR measurements were conducted with the use of the SPECORD M 80 spectrometer (Carl Zeiss, Jena, Germany), in the wavenumber range of 1400–250 cm^{-1}, applying the technique of pressing pellets with KBr at a mass ratio 1:300.

SEM investigations were carried out by means of a scanning electron microscope JSM-1600 (Jeol, Japan).

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Results and discussion

In order to investigate whether the compound belonging to the $M_2FeV_3O_{11}$ family (i.e. $Cd_2FeV_3O_{11}$) is formed in the $CdO–V_2O_5–Fe_2O_3$ system, the equimolar mixture of $FeVO_4$ and $Cd_2V_2O_7$ was heated at 710°C in four stages, each lasting 20 h. The sample's diffraction pattern after the last heating cycle, contained a set of lines typical of CdV_2O_6 (the low-temperature form), $Cd_2V_2O_7$ and also a set of lines which could not be assigned to any known compound crystallizing in lateral systems, building the $CdO–V_2O_5–Fe_2O_3$ system. Thus it was assumed that the set of these lines comes from the new phase that was marked as X. After that another mixture, whose composition corresponded to that of the compound belonging to the $M_3Fe_4V_6O_{24}$ family (i.e. $Cd_3Fe_4V_6O_{24}$), i.e. 37.50 mol% $CdCO_3$, 37.50 mol% V_2O_5 and 25.00 mol% Fe_2O_3, was prepared. Since cadmium orthovanadate(V) is unlikely to exist [17], vanadates could not be applied as the initial reacting substances. The prepared mixture was heated in the following stages: 580°C (20 h)+710°C (20 h·3). In the sample, after the last heating stage, the presence of CdV_2O_6 (the low-temperature form), $Cd_2V_2O_7$ and the X phase, were detected. The type of the phases produced in both samples is then the same, only in the second sample the quantity of the X phase, in relation to the amount of CdV_2O_6 and $Cd_2V_2O_7$, is higher.

The obtained results indicate that in the $CdO–V_2O_5–Fe_2O_3$ system, the $Cd_2FeV_3O_{11}$ and $Cd_3Fe_4V_6O_{24}$ compounds are not formed. However, a new phase demonstrating a different composition and likely to be formed on the cross-section of $FeVO_4–Cd_4V_2O_9$, is produced.

With the view to establishing the composition of the new phase, 7 mixtures of $FeVO_4$ with $Cd_4V_2O_9$ were prepared. The compositions of these mixtures, the way of their heating and the XRD results of the samples after the last heating stage, were presented in Table 1.

The data gathered in Table 1 point out that $FeVO_4$ reacts with $Cd_4V_2O_9$ in the solid-state, resulting in the formation of a new phase. Samples 1 and 2 revealed the presence of $Cd_2V_2O_7$ and Fe_2O_3, besides the X phase, whereas in samples 6 and 7, the presence of $FeVO_4$, apart from the X phase, was identified. The intensity of the lines coming from $FeVO_4$ (in sample 6) and $Cd_2V_2O_7$ and Fe_2O_3 (in sample 2) is negligible. The powder diffraction patterns of samples 3–5 contain only the set of the lines, assigned to the X phase.

On the basis of the presented results it can be assumed that the obtained new phase demonstrates variable composition. Additional tests of $FeVO_4$ as well as $Cd_2V_2O_7$ and Fe_2O_3 detectability towards the X phase were performed by means of XRD method. Sample 4 was mixed with $FeVO_4$ in such proportions so that its composition corresponded to that of the sample 5. On the diffraction pattern of the mixture prepared in this way were recorded the reflections originating from $FeVO_4$. Next sample 4 was blended with $Cd_2V_2O_7$ and Fe_2O_3 in such proportions that its composition corresponded to that of sample 3. The reflections derived from $Cd_2V_2O_7$ and Fe_2O_3 were recorded on the diffraction pattern of this mixture.

The presented results prove that the new phase is characterized by a changeable composition which can be characterized as $Cd_4Fe_{7+x}V_{9+x}O_{37+4x}$, where $-0.5<x<1.5$ ($x=-0.5$ corresponds to sample 2 and $x=1.5$ to sample 6). The compositions of the monophase samples 3–5 correspond to the $x=0$ ($Cd_4Fe_7V_9O_{37}$), $x=0.5$ ($Cd_4Fe_{7.5}V_{9.5}O_{39}$) and $x=1$ ($Cd_4Fe_8V_{10}O_{41}$) values.

Also the synthesis of the new phase was performed by heating the stoichiometric (that is corresponding to the compositions of samples 3–5) mixtures of $CdCO_3$, V_2O_5 and Fe_2O_3 in the following stages: 600°C (20 h)+710°C (20 h).

The DTA curve of $Cd_4Fe_8V_{10}O_{41}$ (Fig. 1) reveals one endothermic effect with its onset temperature equal to 770±5°C. In order to determine the kind of transition beginning at this temperature, sample of $Cd_4Fe_8V_{10}O_{41}$ was heated at 860°C for 2 h and subsequently cooled down rapidly to ambient temperature (at the moment of removing the sample from the furnace it was melted) and subjected to tests by XRD method. The obtained results indicate that $Cd_4Fe_8V_{10}O_{41}$ melts incongruently at 770±5°C. $Cd_2V_2O_7$ and Fe_2O_3 are the solid products of this melting. On the basis of the DTA curves of samples 3

Table 1 Composition of initial mixtures, heating conditions and the results of XRD analysis of samples after the final heating stage

No.	Composition of initial mixtures	Heating conditions	Phases detected
1	$Cd_4V_2O_9$+6$FeVO_4$	730°C (20 h·3)	X, $Cd_2V_2O_7$, Fe_2O_3
2	$Cd_4V_2O_9$+6.5$FeVO_4$		
3	$Cd_4V_2O_9$+7$FeVO_4$	730°C (20 h·4)	X
4	$Cd_4V_2O_9$+7.5$FeVO_4$		
5	$Cd_4V_2O_9$+8$FeVO_4$		
6	$Cd_4V_2O_9$+8.5$FeVO_4$		X, $FeVO_4$
7	$Cd_4V_2O_9$+9$FeVO_4$		

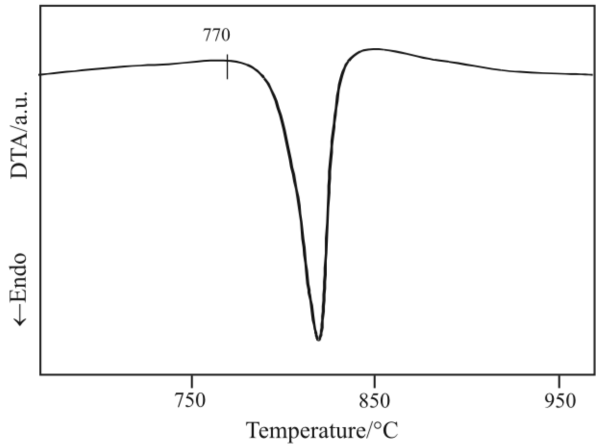

Fig. 1 Fragment of the DTA curve of $Cd_4Fe_8V_{10}O_{41}$

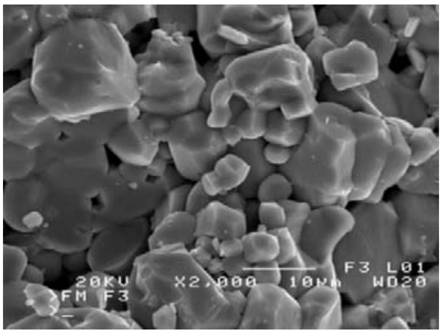

Fig. 2 SEM image of $Cd_4Fe_8V_{10}O_{41}$

and 4 one can state that the melting temperature of the examined phase decreases following the decline of cadmium content in it, that is from 790±5°C (sample 3) through 780±5°C (sample 4) to 770±5°C (sample 5).

Figure 2 presents the SEM image of $Cd_4Fe_8V_{10}O_{41}$, whereas Fig. 3 shows the SEM image of the same sample heated for 2 h at 860°C and rapidly quenched. In the latter case, the crystals have a different morphology from those observed in the sample which was not previously melted.

The $Cd_4Fe_{7+x}V_{9+x}O_{37+4x}$, ($-0.5<x<1.5$) phase has the olive-brown colour. The new phase crystallizes in the triclinic system, the number of stoichiometric units per unit cell is Z=1. Table 2 presents the relationship between the primitive unit cell's parameters and the composition of the tested phase. The volume of the unit cell of the investigated phase decreases together with the decline of the cadmium content. The results of indexing the powder diffraction pattern of $Cd_4Fe_8V_{10}O_{41}$ are given in Table 3. The similarity of both the powder diffraction patterns and the parameters of the unit cell to those typical for the howardevansite type of structure [5] indicate a possible type of structure for the new phase. This assumption is confirmed by the similarity of the IR spectra. Figure 4

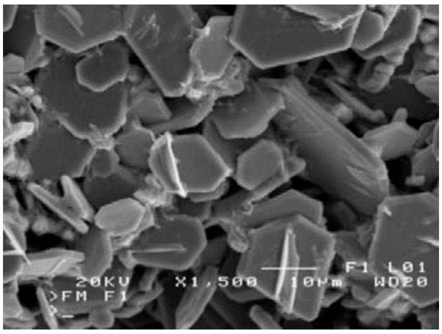

Fig. 3 SEM image of $Cd_4Fe_8V_{10}O_{41}$ heated for 2 h at 860°C and rapidly quenched

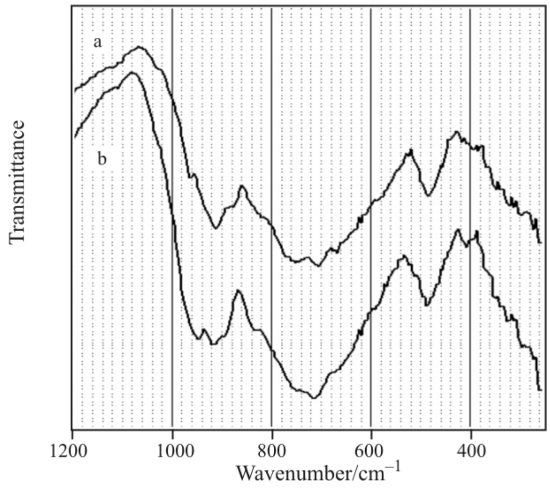

Fig. 4 IR spectra of a – $Cd_4Fe_8V_{10}O_{41}$ and b – $Zn_3Fe_4V_6O_{24}$

Table 2 Lattice parameters of the X phase

Sample	3	4	5
Composition	$Cd_4Fe_7V_9O_{37}$	$Cd_4Fe_{7.5}V_{9.5}O_{39}$	$Cd_4Fe_8V_{10}O_{41}$
a/nm	0.6746(2)	0.6743(2)	0.6734(2)
b/nm	0.8337(4)	0.8335(3)	0.8323(3)
c/nm	0.9886(5)	0.9883(4)	0.9880(4)
α/°	106.14(7)	106.12(5)	106.29(6)
β/°	105.78(6)	105.79(5)	105.69(5)
γ/°	103.13(6)	103.11(5)	103.06(5)
Volume/nm^3	0.4856	0.4852	0.4836

Table 3 Indexing results for the $Cd_4Fe_8V_{10}O_{41}$ powder diffraction pattern (sample 5)

No.	d_{obs}/nm	d_{calc}/nm	*h k l*	*I*/%	No.	d_{obs}/nm	d_{calc}/nm	*h k l*	*I*/%
1	0.7563	0.7550	0 1 0	3	11	0.3775	0.3775	0 2 0	10
2	0.7173	0.7181	0 –1 1	9	12	0.3708	0.3709	1 –2 1	6
3	0.6159	0.6175	–1 0 1	10	13	0.3418	0.3419	1 –1 2	11
4	0.4969	0.4967	–1 1 1	20	14	0.3278	0.3280	–2 0 1	19
5	0.4708	0.4711	1 –1 1	14	15	0.3231	0.3230	2 –1 0	6
6	0.4615	0.4613	–1 –1 1	7	16	0.3168	0.3169	0 –1 3	47
7	0.4426	0.4429	0 0 2	5	17	0.3122	0.3118	–1 –2 1	20
8	0.4150	0.4142	1 1 0	7	18	0.3093	0.3090	0 2 1	100
9	0.4046	0.4043	–1 –1 2	5	19	0.2936	0.2936	–2 1 2	17
10	0.3814	0.3819	1 –2 0	4	20	0.2884	0.2884	2 –2 0	12

(curve a) presents the IR spectrum of $Cd_4Fe_8V_{10}O_{41}$ in comparison with the spectrum of the compound of the howardevansite type structure, i.e. $Zn_3Fe_4V_6O_{24}$ [5] (Fig. 5, curve b). Additionally crystals of $Cd_4Fe_8V_{10}O_{41}$ (Fig. 2) resemble by morphology the crystals of the compounds of the howardevansite type structure, presented earlier [5]. Since the new phase most likely adopts the howardevansite-type structure its formula can be presented as $Cd_{2.34}Fe_{4.68}V_{5.85}O_{24}$ (for the composition $Cd_4Fe_8V_{10}O_{41}$).

Conclusions

$Cd_2FeV_3O_{11}$ and $Cd_3Fe_4V_6O_{24}$ does not exist in the CdO – V_2O_5–Fe_2O_3 system. $FeVO_4$ reacts in the solid-state with $Cd_4V_2O_9$ yielding the new phase whose composition can be described as $Cd_4Fe_{7+x}V_{9+x}O_{37+4x}$, where $-0.5<x<1.5$. This phase melts incongruently depositing solid $Cd_2V_2O_7$ and Fe_2O_3 and its melting temperature declines together with the decrease of cadmium content in it and comprises from 790±5 to 770±5°C. The new phase crystallizes in the triclinic system and its unit cell volume declines together with the decrease of cadmium content in it. The new phase is likely to be of the howardevansite type structure, but is formed in the other cross-section of the three-component system than the phases of the same structure obtained previously.

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