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PHASE RELATIONS IN THE $CoO–V_2O_5–Fe_2O_3$ SYSTEM IN SUBSOLIDUS AREA

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Thermal properties of $Co_2FeV_3O_{11}$ have been reinvestigated. It has been proved that this compound does not exhibit polymorphism. It melts incongruently at the temperature of 770±5°C and the phase with lyonsite type structure is the solid product of this melting. Phase relations in the whole subsolidus area of the $CoO–V_2O_5–Fe_2O_3$ system have been determined. The solidus area projection onto the component concentration triangle plane of this system has been constructed using the DTA and XRD methods. 15 subsidiary subsystems can be distinguished in this system.

Keywords: *$CoO–V_2O_5–Fe_2O_3$ system, DTA, phase relations, XRD*

Introduction

Ternary systems $MO–V_2O_5–Fe_2O_3$ prove to be an interesting object of studies owing to the fact that vanadates(V) which are formed in there, catalyze the oxidation processes of many compounds [1–3]. The investigation into phase relations in such systems has not only a major cognitive value but also often results in obtaining new compounds displaying potential catalytic characteristics.

In one of such systems, i.e. the $ZnO–V_2O_5–Fe_2O_3$ one, vanadates' reactivity in its selected cross-sections was investigated, and additional verifying investigations made it possible to describe the phase relations in its whole subsolidus area [4]. As a result of the all conducted studies it was found that in this system, with all components being involved, two compounds that is the $Zn_2FeV_3O_{11}$ [5] and the $Zn_3Fe_4V_6O_{24}$ [6] one, not previously described, have been formed.

The works conducted on the $CoO–V_2O_5–Fe_2O_3$ ternary system were started by examining the reactivity of vanadates(V) in its three cross-sections, i.e. $FeVO_4–Co_2V_2O_7$, $FeVO_4–Co_3V_2O_8$ and $FeVO_4$–CoO. A new not known before $Co_2FeV_3O_{11}$ compound was obtained as a result of the $FeVO_4$ and $Co_2V_2O_7$ reaction [7]. Also it was established that this compound co-exists at equilibrium with cobalt(II) divanadate(V) [8].

Following the reaction of $FeVO_4$ with $Co_3V_2O_8$ another new phase with the howardevansite (the $NaCuFe_2V_3O_{12}$ mineral) type structure was obtained [9]. The results of our latest research [10] indicate that the composition of the phase with howardevansite type structure (hereafter H-type phase) corresponds with the $Co_{2.616}Fe_{4.256}V_6O_{24}$ formula, therefore it differs from the composition of other phases of the howardevansite type structure, obtained earlier, i.e. $Zn_3Fe_4V_6O_{24}$ and $Mg_3Fe_4V_6O_{24}$ [6].

Literature data report that in the $FeVO_4–Co_3V_2O_8$ system the phase of the lyonsite (the α-$Cu_3Fe_4V_6O_{24}$ mineral) type structure crystallizes. This phase has been relatively recently described [11, 12] and before our studies [10] it was only known that its composition differs from that of the mineral's composition and in all likelihood is changeable. The results of our studies on phase relations in the $FeVO_4–Co_3V_2O_8$ system in the whole range of components concentration made it possible to conclude that the phase with the lyonsite type structure (hereafter the L-type phase) has a wide range of homogeneity with the $Co_{3+1.5x}Fe_{4–x}V_6O_{24}$ ($0.476<x<1.667$) formula [10].

The phase relations in the third cross-section of the $CoO–V_2O_5–Fe_2O_3$ system, i.e. the $FeVO_4$–CoO system, have recently been studied [13]. It was established that this system is the cross-section of the ternary system going across its six subsidiary subsystems. In one of them being at equilibrium there co-exist two solid phases, i.e. the L-type phase and Fe_2O_3, whereas the remaining five ones, have three solid phases each: [$FeVO_4$–H-type phase–Fe_2O_3], [H-type phase–L-type phase–Fe_2O_3], [L-type phase–Fe_2O_3–$CoFe_2O_4$], [L-type phase–$CoFe_2O_4$–$Co_3V_2O_8$] and [$Co_3V_2O_8$–$CoFe_2O_4$–Co_3O_4] [13]. The phase relations in the [$Co_3V_2O_8$–$CoFe_2O_4$–Co_3O_4] subsidiary subsystem were examined only in the range of temperatures from 560°C (decomposition of the used $CoCO_3$) to 750°C. Heating was conducted in the air atmosphere, therefore

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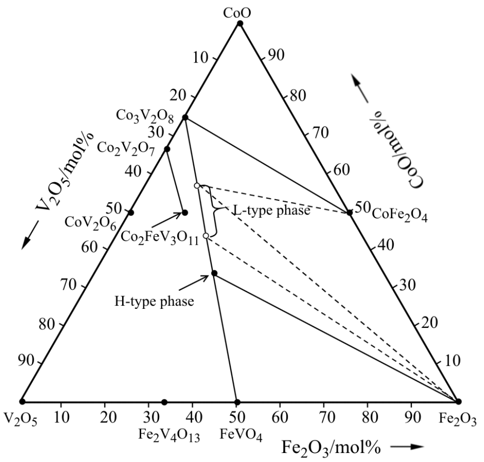

Fig. 1 Preliminary dividing of the subsolidus area of the system CoO–V_2O_5–Fe_2O_3

Co_3O_4, instead of CoO was identified in the samples in this range of temperatures. The processes which took place during the heating above 750°C have not been thoroughly determined and are being in the process of further investigation [13].

The findings of the investigations into the three systems, being the cross-sections of the CoO–V_2O_5–Fe_2O_3 [8, 10, 13] system allowed a preliminary dividing of part of the subsolidus area of this system into subsidiary subsystems (Fig. 1). The lines connecting the L-type phase with other compounds were designated with a dashed line, since the samples whose compositions were marked as ○, next to the L-type phase, the H-type phase and $Co_3V_2O_8$ respectively were identified with the XRD method, however in quantities on the verge of detection. The composition of these samples has been described by the $Co_{3+1.5x}Fe_{4-x}V_6O_{24}$ formula, where x=0.476 and 1.667, respectively. The proposed division did not include the polygons labeled by the following phases: $Co_3V_2O_8$, the L-type phase, the H-type phase, $FeVO_4$, $Fe_2V_4O_{13}$, V_2O_5, CoV_2O_6 and $Co_2V_2O_7$.

The aim of this work was to determine the phase relations in the whole subsolidus area of the CoO–V_2O_5–Fe_2O_3 system. Also the results of the re-investigations into the thermal properties of $Co_2FeV_3O_{11}$, which turned out to be necessary in the light of the new information regarding the existence of the phase of the lyonsite type structure [10], were presented.

Experimental

The reacting substances used in the research were as follows: Fe_2O_3 (p.a., POCh, Poland), V_2O_5 (p.a., Riedel-de Haën, Germany) and $CoCO_3$ (p., Fluka Chemie, Switzerland). The reactions were carried out by the conventional method of calcining samples. Appropriate portions of the reacting substances, after the homogenization and forming them into pellets, were heated in the air atmosphere for several stages until the state of equilibrium was obtained. During each heating stage the samples were gradually cooled down in the furnace to ambient temperature, ground and examined by the XRD method, some selected samples also by the DTA one. In order to carry out the verifying investigations the separately obtained: $FeVO_4$, $Fe_2V_4O_{13}$, CoV_2O_6, the H-type phase ($Co_{2.616}Fe_{4.256}V_6O_{24}$), the L-type phase ($Co_{3.827}Fe_{3.449}V_6O_{24}$) were applied. The mixtures of the appropriate phases, after their homogenization and forming into pellets, were heated in two 20 h cycles at the temperatures by a few dozen °C lower than that of their melting, designated on the basis of the DTA curves of those mixtures. Next, after they were cooled down to ambient temperature and ground, their composition was examined by the XRD method.

The DTA measurements were performed by means of the Paulik–Paulik–Erdey type derivatograph (MOM, Hungary). The investigations were conducted in the air atmosphere in the temperature range 20–1000°C at a heating rate of 10°C min^{-1}. Samples of 500 mg by mass were placed in quartz crucibles. The accuracy of reading the temperatures of thermal effects on the DTA curves – as determined on the basis of repetitions – amounted to ±5°C.

The composition of the samples was determined on the basis of their powder diffraction patterns [14–17] obtained by means of an X-ray DRON-3 diffractometer (Bourevestnik, Sankt Petersburg, Russia). A cobalt tube (CoK_α) equipped with an iron filter was used as a source of radiation. The identification of the phases was conducted with the aid of the XRD characteristics given in the PDF cards [18] and the data published in the works [7, 9, 11, 12]. The powder diffraction pattern of the L-type phase was indexed by applying the Refinement program of the DHN/PDS package, using α-Al_2O_3 as the internal standard.

Results and discussion

The studies were commenced by verifying the thermal properties of $Co_2FeV_3O_{11}$ first. The results of the earlier works [7] indicated that $Co_2FeV_3O_{11}$ has two polymorphous modifications, and the temperature of the phase transition α-→β- is 770±5°C [7]. On the basis of the indexing results of the β-$Co_2FeV_3O_{11}$ powder diffraction pattern it was found that this phase crystallizes in the triclinic system [7]. The diffraction pattern of the β-$Co_2FeV_3O_{11}$ modification is a set of lines, the majority of which, taking both their position and intensity into consideration, correspond to the phase of the lyonsite type structure [11, 12]. Additional reflections, characterized by low intensity can be regarded as belonging to the diffraction pattern of V_2O_5. In order to define conclusively whether these reflections are connected with the presence of vanadium(V) oxide or belong to the set of lines characterizing β-$Co_2FeV_3O_{11}$ the β-$Co_2FeV_3O_{11}$ sample was subjected to the activity of the KOH solution with the concentration of 6 mol dm^{-3} for 1 h (stirring vigorously), next after rinsing KOH with water and drying, it was examined with the XRD method. This time only the lines characterizing the phase of the lyonsite type structure were recorded on the diffractogram of the examined sample. The obtained results indicate that due to V_2O_5 good solubility in KOH, the vanadium(V) oxide was removed from the sample. Therefore it can be concluded that the $Co_2FeV_3O_{11}$ compound does not exhibit polymorphism.

'β-$Co_2FeV_3O_{11}$' was obtained in such a way: a sample of the $Co_2FeV_3O_{11}$ was heated at 900°C for 3 h, i.e. at a temperature higher by 130°C than the onset temperature of the first effect recorded on the DTA curve of $Co_2FeV_3O_{11}$ (i.e. 770±5°C) and then this sample was rapidly quenched. The diffraction pattern of this 'frozen' sample contained a set of diffraction lines characteristic for the phase of the lyonsite type structure ($Co_{3+1.5x}Fe_{4-x}V_6O_{24}$ – melting temperature 970–990±5°C depending on its composition) [10] and for V_2O_5 (melting temperature about 630°C). Therefore it can be concluded that $Co_2FeV_3O_{11}$ melts incongruently at 770±5°C and the phase of the lyonsite type structure is the solid product of this melting:

$$Co_2FeV_3O_{11(s)} \leftrightarrow Co_{3+1.5x}Fe_{4-x}V_6O_{24(s)}+\text{liquid}$$

On the basis of the powder diffraction pattern indexing results of the forming phase it was found that it crystallizes in the orthorhombic system, where the parameters of its unit cell are: a=0.4998(3) nm, b=1.0211(1) nm, c=1.7199(3) nm. Following the earlier investigations [10] it was established how the composition of the phase of the lyonsite type structure affects the size of the unit cell's parameters. This dependence makes it possible to assess that the composition of the phase being formed as a result of $Co_2FeV_3O_{11}$ melting can be described by the $Co_{3+1.5x}Fe_{4-x}V_6O_{24}$ formula, where x is found within the $1<x<1.524$ limits.

The suggested division of part of the subsolidus area of the CoO–V_2O_5–Fe_2O_3 system into subsidiary subsystems (Fig. 1) required experimental verification, whereas establishing the phase relations in the polygon described by means of the following phases: $Co_3V_2O_8$, the L-type phase, the H-type phase, $FeVO_4$, $Fe_2V_4O_{13}$, V_2O_5, CoV_2O_6 and $Co_2V_2O_7$ called for supplementary investigations. For this purpose 12 mixtures of $CoCO_3$, V_2O_5 and Fe_2O_3 were prepared with their compositions confined within the region designated by the $Co_3V_2O_8$, the L-type phase, CoV_2O_6 and $Co_2V_2O_7$ phases (samples 1–9), as well as the regions corresponding to some proposed subsidiary subsystems (samples 10–12). Table 1 presents the compositions of the prepared mixtures, the conditions of their heating and also the results of the analysis, conducted by means of the XRD method, of the samples obtained after the last stage of heating. The composi-

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

No.	Composition of initial mixtures/mol%			Heating conditions	Phases detected in the samples on the base of their powder diffraction patterns
	CoO	V_2O_5	Fe_2O_3		
1	66.00	31.00	3.00	580°C (20 h)·2+660°C (20 h)+ 810°C (20 h)·2	$Co_3V_2O_8$, $Co_2V_2O_7$, L-type phase
2	55.00	34.00	11.00	580°C (20 h)·2+620°C (20 h)+ 660°C (20 h)·3	$Co_2V_2O_7$, L-type phase, $Co_2FeV_3O_{11}$
3	55.00	40.00	5.00		$Co_2V_2O_7$, $Co_2FeV_3O_{11}$, CoV_2O_6
4	50.00	43.00	7.00		$Co_2FeV_3O_{11}$, CoV_2O_6
5	48.50	37.88	13.62	580°C (20 h)·2+600°C (20 h)+ 620°C (20 h)·2	$Co_2FeV_3O_{11}$, CoV_2O_6, L-type phase
6	46.95	41.31	11.74		CoV_2O_6, L-type phase
7	47.62	36.39	15.99	580°C (20 h)·2+600°C (20 h)+ 680°C (20 h)·2	L-type phase, $Co_2FeV_3O_{11}$
8	53.00	34.52	12.48		L-type phase, $Co_2FeV_3O_{11}$
9	50.50	34.50	15.00		L-type phase, $Co_2FeV_3O_{11}$
10	50.00	31.00	19.00	580°C (20 h)·2+600°C (20 h)+ 680°C (20 h)+910°C (20 h)·2	L-type phase, Fe_2O_3
11	40.00	10.00	50.00	580°C (20 h)·2+660°C (20 h)+ 680°C (20 h)+910°C (20 h)·2	L-type phase, Fe_2O_3, $CoFe_2O_4$
12	10.00	30.00	60.00	580°C (20 h)·2+600°C (20 h)+ 680°C (20 h)+780°C (20 h)·2	H-type phase, $FeVO_4$, Fe_2O_3

tions of samples 6–8 were selected in such a way that they were situated on the line joining $Co_2FeV_3O_{11}$ or CoV_2O_6 with the L-type phase displaying the compositions corresponding to the terminal samples where only the L-type phase was identified.

Determining the phase relations in the polygon described with the following phases: CoV_2O_6, the L-type phase, the H-type phase, $FeVO_4$, $Fe_2V_4O_{13}$ and V_2O_5 required a different way of approaching. When the reactivity of $FeVO_4$ towards $Co_2V_2O_7$ was examined, it was noted that the samples containing over 60.00% mol $FeVO_4$ in the initial mixtures, comprised a mixture of $FeVO_4$, CoV_2O_6 and the L-type phase after a reaction [8]. The results of the studies on phase relations in the $FeVO_4$–$Co_3V_2O_8$ system [10] indicated that in this range of concentrations the H-type phase should be formed. This phase was not detected in any of the samples [8]. The temperature of heating those samples is probably the key to the situation. The H-type phase synthesis is conducted at a relatively high temperature, i.e. 780°C [9, 10]. The phase is not formed at all or in a very small quantity at the temperature below 700°C [10]. Due to the fact that in the samples displaying the compositions belonging to the $FeVO_4$–$Co_2V_2O_7$ cross-section, a relatively low-melting CoV_2O_6 is formed, they could not be heated at the temperatures above 700°C. The presence of CoV_2O_6, $Fe_2V_4O_{13}$ and V_2O_5 (melting temperatures about 730, 670 and 630°C, respectively) in the polygon described with the following phases: CoV_2O_6, the L-type phase, the H-type phase, $FeVO_4$, $Fe_2V_4O_{13}$ and V_2O_5, limits the temperature of heating the samples, thus making forming the H-type phase impossible. A similar problem occurred when phase relations in similar $FeVO_4$–$Zn_2V_2O_7$ [19] and $FeVO_4$–$Mg_2V_2O_7$ [20] systems were examined. The synthesis of the phases with the howardevansite type structure formed in these systems also faced difficulties. It was decided that the phase relations in the area marked by the following phases: CoV_2O_6, the L-type phase, the H-type phase, $FeVO_4$, $Fe_2V_4O_{13}$ and V_2O_5 were to be determined by preparing and heating the mixtures of the ready made phases with appropriately selected compositions.

The first stage consisted in deciding which compounds of the studied polygon the H-type phase stays at equilibrium with. Three mixtures containing the H-type phase and respectively $Fe_2V_4O_{13}$, CoV_2O_6 or V_2O_5, were prepared. The compositions of the given mixtures are presented in Table 2 (samples 1–3). These mixtures were heated in two 20 h cycles at 580°C. The compositions of samples 1 and 2 did not change after heating. This proves that the composition of the initial mixtures corresponded with the phases co-existing at equilibrium. The composition of sample 3 revealed a small quantity of CoV_2O_6 which proves that the components of the prepared mixture react one with another, thus they are not at equilibrium. On the basis of the obtained results another possibility can be projected, namely that CoV_2O_6 co-exists at equilibrium with $Fe_2V_4O_{13}$. This assumption as well as all the previously obtained results lead to a presumption that there are the following subsidiary subsystems: [CoV_2O_6–$Fe_2V_4O_{13}$–V_2O_5], [CoV_2O_6–$Fe_2V_4O_{13}$–H-type phase], [CoV_2O_6–L-type phase–H-type phase] and [H-type phase–$FeVO_4$–$Fe_2V_4O_{13}$] in the polygon determined by the phases: CoV_2O_6, the L-type phase, the H-type phase, $FeVO_4$, $Fe_2V_4O_{13}$ and V_2O_5. With the view to confirming the assumed division of the examined polygon experimentally, five samples being the mixtures of the phases, which probably remain at equilibrium, were prepared. The compositions of those mixtures are demonstrated in Table 2 (samples 4–8). The mixtures were heated in two 20 h cycles at the temperatures being a few dozen °C lower than the onset temperatures of their melting. The compositions of the samples did not change, which means that the compositions of the initial mixtures corresponded with the phases remaining at equilibrium.

Having taken all the conducted investigations into consideration, a phase diagram of the CoO–V_2O_5–Fe_2O_3 system in the subsolidus area was prepared. Onset temperatures of the first endothermic effects read on the DTA curves of the samples corresponding to a given

Table 2 Composition of verifying mixtures and their recounting for CoO–V_2O_5–Fe_2O_3 system components

No.	Composition of verifying mixtures	Composition of verifying mixtures in terms of components of CoO–V_2O_3–Fe_2O_3 system/mol%		
		CoO	V_2O_5	Fe_2O_3
1	H-type phase, $Fe_2V_4O_{13}$	15.00	54.28	30.72
2	H-type phase, CoV_2O_6	43.57	45.54	10.89
3	H-type phase, V_2O_5	22.52	59.16	18.32
4	CoV_2O_6, $Fe_2V_4O_{13}$	22.52	59.16	18.32
5	CoV_2O_6, $Fe_2V_4O_{13}$, V_2O_5	20.00	70.00	10.00
6	CoV_2O_6, $Fe_2V_4O_{13}$, H-type phase	30.00	50.00	20.00
7	H-type phase, CoV_2O_6, L-type phase	42.00	40.00	18.00
8	H-type phase, $Fe_2V_4O_{13}$, $FeVO_4$	15.00	49.00	36.00

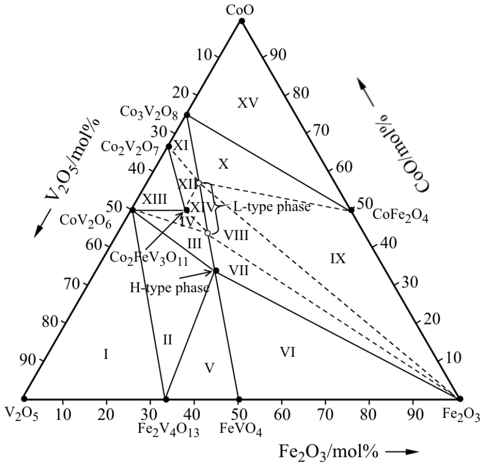

Fig. 2 Projection of solidus surface onto the plane of component concentration triangle of the system CoO–V_2O_5–Fe_2O_3

area were assumed as the melting temperatures of the phase mixtures remaining at equilibrium in a given area. Figure 2 presents the projection of the solidus surface onto the plane of the component concentration triangle of this system. All the lines linking the L-type phase with other compounds were marked with a dashed line. It can be concluded from the presented diagram that in the CoO–V_2O_5– Fe_2O_3 system there can be distinguished 15 subsidiary subsystems where the following phases co-exist at equilibrium:

	System	$T_{melting}$
I	V_2O_5–$Fe_2V_4O_{13}$–CoV_2O_6	620±5°C
II	CoV_2O_6–$Fe_2V_4O_{13}$–H-type phase	640±5°C
III	CoV_2O_6–H-type phase–L-type phase	640±5°C
IV	CoV_2O_6–L-type phase–$Co_2FeV_3O_{11}$	650±5°C
V	$Fe_2V_4O_{13}$–$FeVO_4$–H-type phase	670±5°C
VI	$FeVO_4$–Fe_2O_3–H-type phase	830±5°C
VII	Fe_2O_3–H-type phase–L-type phase	860±5°C
VIII	Fe_2O_3–L-type phase	970±5°C
IX	Fe_2O_3–L-type phase–$CoFe_2O_4$	970±5°C
X	L-type phase–$CoFe_2O_4$–$Co_3V_2O_8$	990±5°C
XI	L-type phase–$Co_3V_2O_8$–$Co_2V_2O_7$	860±5°C
XII	L-type phase–$Co_2V_2O_7$–$Co_2FeV_3O_{11}$	760±5°C
XIII	$Co_2V_2O_7$–$Co_2FeV_3O_{11}$–CoV_2O_6	725±5°C
XIV	$Co_2FeV_3O_{11}$–L-type phase	750±5°C
XV	$Co_3V_2O_8$–$CoFe_2O_4$–Co_3O_4*	>1000°C

*in the temperature range 560–750°C

Conclusions

- The $Co_2FeV_3O_{11}$ compound does not exhibit polymorphism and melts incongruently at 770±5°C, the temperature which was earlier recognized as the temperature of polymorphous transformation. The L-type phase is the solid product of the melting.
- 15 subsidiary subsystems can be distinguished in the CoO–V_2O_5–Fe_2O_3 system. In two of them there co-exist two solid phases at equilibrium, whereas the remaining 13 ones have three solid phases each.

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