The synthesis and some properties of new compound $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$

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Abstract A new compound with the formula $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ has been obtained as a result of a solid-state reactions occurring during heating the mixtures both of oxides: CuO , V_2O_5 , Fe_2O_3 and vanadates: $\text{Cu}_5\text{V}_2\text{O}_{10}$, $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$. The DTA measurements were used to choose the heating temperatures as well as for determination of thermal stability of the new compound. $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ melts incongruently at $790 \pm 5^\circ\text{C}$. The new phase crystallizes in the monoclinic system. The indexing results and the calculated unit cell parameters for $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ are given. Its infra-red spectrum and image obtained by means of an electron scanning microscope are presented.

Keywords Copper iron vanadate · DTA · Solid-state reaction · XRD

Introduction

Vanadates(V) of di- and trivalent metals belong to the few catalysts which are able to stop the process of oxidation of some organic compounds at the intermediate stage, e.g. corresponding to olefins or aldehydes. It is known, for example, that copper(II) vanadates(V) are catalytically active in the reaction of oxidative dehydrogenation of isobutane to isobutene [1], whilst iron(III) orthovanadate(V) catalyses methanol oxidation to formaldehyde [2]. In view of the above, it can be expected that the phases

forming as a result of reactions of the above vanadates(V) will also prove attractive from the catalytic application point of view. Thus, the system $\text{CuO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$ seems as a reasonable choice in the search for new potential catalysts of selective oxidation of organic compounds.

It is known that in one of the cross sections of the $\text{CuO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$ system, i.e. in the system $\text{FeVO}_4-\text{Cu}_3\text{V}_2\text{O}_8$, a double vanadate(V) of the formula $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ is formed [3–5]. This compound is met in two crystallographic modifications. The α - $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ form is a mineral called lyonsite [6]. The synthesis of $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ by the conventional solid-state reaction leads to its another form, i.e. β - $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [3–5] whose structure is like that of mineral howardevansite, $\text{NaCuFe}_2\text{V}_3\text{O}_{12}$ [7]. According to Belik et al. [8], the phase of the lyonsite type structure can be obtained by the conventional method of sintering, but the phase thus obtained has a composition different from that describing the mineral, and moreover, it has a certain range of homogeneity as expressed by $\text{Cu}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$ ($0.667 \leq x < 0.778$). The two minerals were discovered in the summit crater fumaroles of the Izalco volcano [6, 7]. The phases of the structures of lyonsite and howardevansite also form in other analogous ternary systems [8–11].

Belik et al. [8] studied the reactivity of oxides only for a limited range of concentrations of $\text{FeVO}_4-\text{Cu}_3\text{V}_2\text{O}_8$ system, i.e. from 14.29 to 50.00 mol% $\text{Cu}_3\text{V}_2\text{O}_8$ in the initial mixtures. Interestingly, diffractograms of some samples containing from 30.15 to 50.00 mol% $\text{Cu}_3\text{V}_2\text{O}_8$, have revealed a number of unidentified reflexes besides those characteristic for $\text{Cu}_2\text{V}_2\text{O}_7$ and for lyonsite structure phase [8]. This observation could mean that besides the phases of lyonsite and howardevansite structures, there is one more phase in the ternary system $\text{CuO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$ in which all components are engaged. The authors [8] have not

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attempted to determine of the composition of this unknown phase.

The aim of the study presented was to establish the composition of the new phase forming in the $\text{CuO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ system and determine its some physicochemical properties.

Experimental

Samples were obtained from the following oxides: CuO (p.a., Fluka), V_2O_5 (p.a., Riedel-de Haën), and $\alpha\text{-Fe}_2\text{O}_3$ (p.a., POCh). Only one sample was prepared from vanadates: $\text{Cu}_5\text{V}_2\text{O}_{10}$ [12, 13] and $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [3–5]. These vanadates were obtained as a result of sintering the stoichiometric mixtures of appropriate oxides in the following stages:

- synthesis of $\text{Cu}_5\text{V}_2\text{O}_{10}$: $560\text{ }^\circ\text{C}(20\text{ h}) + 750\text{ }^\circ\text{C}(20\text{ h}) \times 2$
- synthesis of $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$: $560\text{ }^\circ\text{C}(20\text{ h}) + 590\text{ }^\circ\text{C}(20\text{ h}) + 610\text{ }^\circ\text{C}(20\text{ h}) + 625\text{ }^\circ\text{C}(20\text{ h})$ [4]

The XRD characteristics of $\text{Cu}_5\text{V}_2\text{O}_{10}$ and $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ obtained this way were consistent with PDF data (cards: 70-1326 and 80-0220, respectively).

The reactions, both amongst oxides as well as between $\text{Cu}_5\text{V}_2\text{O}_{10}$ and $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, were carried out in the solid state by conventional method of sintering samples [14–17]. The initial mixtures of reactants, after homogenising by grinding, were heated in porcelain crucibles in the atmosphere of air for several stages until the state of equilibrium was attained. On completion of each heating stage, the samples were gradually cooled down in furnace to room temperature, ground and investigated by XRD method with respect to their compositions. Some of the samples were investigated by DTA method too. This procedure was repeated until the compositions of the samples did not change after two consecutive heating stages. The heating temperatures were about $60\text{ }^\circ\text{C}$ below the melting points of the samples, as determined by DTA method. The melting temperatures of the samples were read as the onset temperature of the first endothermic effect recorded in the DTA curve of given sample. Accuracy of reading these temperatures ($\pm 5\text{ }^\circ\text{C}$) was determined by repetitions.

The DTA/TG investigations (the Paulik–Paulik–Erdey type derivatograph; MOM, Hungary) were performed in air atmosphere at a rate of $10\text{ }^\circ\text{C min}^{-1}$. Samples of 500 mg were heated in quartz crucibles in the temperature range $20\text{--}1,000\text{ }^\circ\text{C}$.

Samples were studied by means of an X-ray diffractometer HZG4/A2 (Carl Zeiss, Germany). The source of radiation used was a copper tube equipped with a nickel filter. The identification of phases occurring in the samples

was performed on the base of their XRD characteristics contained in the PDF cards. The powder diffraction pattern of the new compound was indexed by means of the Dicvol program [18], using $\alpha\text{-Al}_2\text{O}_3$ as the internal standard. The parameters of the unit cell were refined by the Refinement program of DHN/PDS package.

The density of the new phase was determined using the method described in the work [19].

The IR measurement (Specord M 80; Carl Zeiss, Germany) was conducted in the wavenumber range of $1,400\text{--}250\text{ cm}^{-1}$, applying the technique of pressing pellets of the new compound with KBr in a ratio 1:300 by weight.

The investigations by SEM/EDX methods were carried out by means of an electron scanning microscope (JSM-1600, Jeol, Japan) with an X-ray energy dispersive analysis (ISIS-300, Oxford).

Results and discussion

The compositions of the samples prepared for investigation, the methods of their heating, and XRD analysis results of these samples after their last heating stage are given in Table 1. The position of the investigated samples in the component concentration triangle of the $\text{CuO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ system is shown in Fig. 1. The position of $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [3–5] and the lyonsite structure phase [8] are also marked.

The study was started with checking if the composition of the unknown phase (hereafter X-phase) corresponds to the formula Cu_2FeVO_6 , as according to the literature in some analogous ternary systems, the compounds of the general formula M_2AVO_6 are formed, e.g. Ni_2FeVO_6 [20], Cu_2BiVO_6 [21], Cd_2InVO_6 [22].

A mixture of the composition corresponding to the formula Cu_2FeVO_6 was prepared (Table 1 sample 1). The diffractogram of this sample, being in the state of equilibrium, showed a set of reflexes which could not have been assigned to any of the known phases forming in the $\text{CuO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ system, besides the reflexes attesting to the presence of $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$. It was assumed that this set of reflexes characterises the unknown X-phase. According to the results, the sample was not monophase, and so the composition of the new phase must be different from that described by the formula Cu_2FeVO_6 .

In the ternary system, the composition of the forming phase corresponds often to the point of intersection of the system's cross sections. Three mixtures were prepared for the study. Their compositions (Table 1) correspond to the intersection points of the cross section of $\text{Cu}_3\text{V}_2\text{O}_8\text{-Fe}_2\text{O}_3$ with the systems: $\text{FeVO}_4\text{-Cu}_5\text{V}_2\text{O}_{10}$ (sample 2), $\text{Cu}_5\text{V}_2\text{O}_{10}\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ (sample 3) and $\text{FeVO}_4\text{-Cu}_{11}\text{V}_6\text{O}_{26}$ (sample 4). According to the above data, the new phase is most probably formed in the $\text{Cu}_5\text{V}_2\text{O}_{10}\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ system.

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

No.	Composition of initial mixtures (mol%)			Heating conditions	Phases at equilibrium state
	CuO	V_2O_5	Fe_2O_3		
1	66.66	16.67	16.67	560 °C (20 h) + 600 °C (20 h) + 700 °C (20 h) + 720 °C (20 h) × 2	X, Fe_2O_3 , $\text{Cu}_5\text{V}_2\text{O}_{10}$
2	68.18	22.73	9.09		X, Fe_2O_3 , $\text{Cu}_5\text{V}_2\text{O}_{10}$
3	69.23	23.08	7.69		X, $\text{Cu}_5\text{V}_2\text{O}_{10}$
4	71.74	23.91	4.35		X, $\text{Cu}_3\text{V}_2\text{O}_8$, $\text{Cu}_{11}\text{V}_6\text{O}_{26}$
5	67.39	23.91	8.70		X, $\text{Cu}_5\text{V}_2\text{O}_{10}$
6	65.00	25.00	10.00		X
7	62.96	25.93	11.11		X, lyonsite-type phase
8	65.00	23.00	12.00		X, Fe_2O_3 , $\text{Cu}_5\text{V}_2\text{O}_{10}$
9	65.33	26.67	8.00		X, $\text{Cu}_2\text{V}_2\text{O}_7$

The composition of sample 3 expressed in the components of the $\text{Cu}_5\text{V}_2\text{O}_{10}$ – $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ system corresponds to the $\text{Cu}_5\text{V}_2\text{O}_{10}$: $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ ratio of 3:1. At the equilibrium

Fig. 1 The position of $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, lyonsite type phase and the investigated samples in the component concentration triangle of the CuO – V_2O_5 – Fe_2O_3 system

state, there is an excess of $\text{Cu}_5\text{V}_2\text{O}_{10}$ in this sample. Two other samples were prepared of the compositions corresponding to the $\text{Cu}_5\text{V}_2\text{O}_{10}$: $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ ratio of 2.5:1 (sample 5) and 2:1 (sample 6). In sample 6, at the state of equilibrium neither the initial reagents nor any of the phases known to form in the CuO – V_2O_5 – Fe_2O_3 were found. The diffractogram of this sample showed only the set of reflexes assumed to correspond to the unknown X-phase.

Three more samples were prepared of compositions similar to that of sample 6 (Table 1, samples 7–9). In all these samples at the state of equilibrium, the presence of X-phase along with the other phases known to form in the ternary system studied was confirmed.

Analysis of all above data permits concluding that as a result of heating a mixture of the composition 65.00% mol CuO , 25.00% mol V_2O_5 and 10.00% mol Fe_2O_3 (sample 6), a new phase has been formed whose composition can be described by the formula $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$. Hence, the new phase is formed in the solid-state reaction according to the equation:

The new phase was also synthesised using as initial reagents the components of the system $\text{Cu}_5\text{V}_2\text{O}_{10}$ –

Table 2 Indexing results for the $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ powder diffraction pattern

No.	d_{obs}/nm	$d_{\text{calc}}/\text{nm}$	h	k	l	$I/\%$
1	0.8916	0.8894	0	2	0	44
2	0.5724	0.5725	−1	2	1	8
3	0.5372	0.5366	2	2	0	9
4	0.4455	0.4453	2	0	1	14
5	0.4353	0.4350	3	1	0	6
6	0.3711	0.3710	2	4	0	16
7	0.3663	0.3660	−2	1	2	24
8	0.3542	0.3543	−2	4	1	16
9	0.3362	0.3363	−3	0	2	34
10	0.3227	0.3227	3	2	1	3
11	0.3147	0.3147	2	4	1	13
12	0.3039	0.3041	−2	5	1	40
13	0.2967	0.2965	0	6	0	100
14	0.2749	0.2750	−5	1	1	15
15	0.2692	0.2692	5	0	0	3
16	0.2658	0.2657	−5	2	1	10
17	0.2593	0.2594	−1	0	3	4
18	0.2483	0.2482	0	1	3	22
19	0.2467	0.2468	2	6	1	18
20	0.2439	0.2439	−5	2	2	24
21	0.2361	0.2361	−1	6	2	6
22	0.2298	0.2298	−3	3	3	8
23	0.2274	0.2275	1	2	3	12
24	0.2243	0.2243	6	0	0	7
25	0.2225	0.2224	4	6	0	35

$\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$. A mixture of the composition 66.67 mol% $\text{Cu}_5\text{V}_2\text{O}_{10}$ and 33.33 mol% $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ was heated for two 20 h stages at 720 °C. The diffractogram of the sample taken after the first 20 h of heating showed only the set of reflexes characteristic for the phase $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$. Therefore, the new phase was obtained in the solid-state reaction according to the equation:

$\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ has a brown sort of colour, its density amounts to $d_{\text{obs}} = 3.97(5) \text{ g/cm}^3$. The powder diffractogram of the new phase was subjected to indexing, results of which are given in Table 2. $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ crystallizes in the monoclinic system, its primitive unit cell parameters are as follows: $a = 1.3976(2) \text{ nm}$, $b = 1.7788(3) \text{ nm}$, $c = 0.7810(1) \text{ nm}$, $\beta = 105.65(2)^\circ$. The unit cell volume $V = 1.8696 \text{ nm}^3$; the number of stoichiometric units in the unit cell $Z = 2$; the XRD calculated density $d = 4.02 \text{ g/cm}^3$.

A SEM image of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ (Fig. 2) shows the presence of only one of crystals' habit. Crystals of the new compound are differentiated in size. The sizes of the larger

Fig. 2 SEM image of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ **Fig. 3** IR spectrum of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$

crystals are of the order of 20 μm , whereas the sizes of the smaller crystals do not often exceed 10 μm . The results of experimental determination of composition by EDX analysis of monophase sample showed that the Cu:Fe:V ratios are near 13:4:10 (on average: 48.28 at% Cu, 13.97 at% Fe and 37.75 at% V) and correspond to the values from formula of the new compound, i.e.: 48.15 at% Cu, 14.81 at% Fe and 37.04 at% V.

Figure 3 shows the IR spectrum of the new compound. In the light of information on the literature, the absorption bands located in the wave number range of 1,050–600 cm^{-1} can be ascribed to the stretching vibrations of the V–O bonds in the VO_4 and VO_5 polyhedra [23–26]. They can be due to the stretching vibrations of the Fe–O bonds in the FeO_5 and FeO_4 polyhedra, too [24, 26, 28]. The absorption bands recorded in the

Fig. 4 Fragment of DTA curve of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$

remaining wave number, i.e. $600\text{--}300\text{ cm}^{-1}$ can be associated with stretching vibrations of the M–O bonds within FeO_6 and CuO_x polyhedra as well as with bending vibrations of O–V–O bonds [24–28].

The DTA curve recorded for $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ (Fig. 4) shows two endothermic effects beginning at temperatures close to each other: at $790 \pm 5\text{ °C}$ and about 800 °C , respectively. To establish the type of transformation causing these effects, three samples of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ compound were prepared. They were additionally heated for 2 h at different temperatures from the range $780\text{--}820\text{ °C}$, and then rapidly cooled to room temperature, and then they were subjected to XRD study. The first sample was heated at 780 °C (close to the beginning of the first endothermic effect), the second at 800 °C (just after the beginning of the effect), whilst the third sample was heated at 820 °C (at the temperature corresponding to a half of the height of the first endothermic effect). On removal from the furnace, the samples heated at 800 or 820 °C were molten, whilst in the one heated at 780 °C , the liquid was not observed. The diffractogram of the sample heated at 780 °C did not differ from that of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$. The diffractograms of the samples heated at 800 and 820 °C were the same and did not show reflexes characteristic for $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$. Thus, it was concluded that the endothermic effect beginning at $790 \pm 5\text{ °C}$ is related to melting of the new compound and the process of its melting was characterised as incongruent. The only solid phase, occurring in the $\text{CuO}\text{--}\text{V}_2\text{O}_5\text{--}\text{Fe}_2\text{O}_3$ system, identified in the samples after their melting, was $\alpha\text{-Fe}_2\text{O}_3$ with a melting point above $1,000\text{ °C}$. As indicated by the course of the DTA curve of the new compound, it melts

with separation of the second solid phase of melting point similar to that of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$. Because of the closeness of temperatures of these two endothermic effects in the experiment conditions (“freezing” at 780 , 800 and 820 °C); no reliable assignment of the second product of melting of the new compound has been made. At this stage of the study, it can be supposed that it is $\text{Cu}_5\text{V}_2\text{O}_{10}$ with the melting point at $805 \pm 5\text{ °C}$. Studies aimed at resolving this question will be continued.

Conclusions

Reaction occurring in the solid state between oxides CuO , V_2O_5 and Fe_2O_3 , taken at a molar ratio 13:5:2, yielded new compound with the formula $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$. This new phase crystallizes in the monoclinic system, and its unit cell parameters are as follows: $a = 1.3976(2)\text{ nm}$, $b = 1.7788(3)\text{ nm}$, $c = 0.7810(1)\text{ nm}$, $\beta = 105.65(2)^\circ$. $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ melts incongruently at $790 \pm 5\text{ °C}$. The new compound can be also obtained as a result of solid–state reaction between $\text{Cu}_5\text{V}_2\text{O}_{10}$ and $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, taken at a molar ratio 2:1.

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