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$Pb_2Fe_2V_4O_{15}$—A new phase forming in the system $FeVO_4$–$Pb_2V_2O_7$

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ABSTRACT

A new iron lead vanadate $Pb_2Fe_2V_4O_{15}$ forming in the system $FeVO_4$–$Pb_2V_2O_7$ has been synthesized. It crystallizes in the triclinic system and melts incongruently at $640 \pm 5\,^{\circ}C$. The IR spectrum and the SEM images of the new phase are presented. A phase diagram of the system $FeVO_4$–$Pb_2V_2O_7$ up to the solidus line has been constructed.

1. Introduction

It is known from the literature information that some vanadates(V) possessing in their structure isolated VO_4 tetrahedra (orthovanadates) or V_2O_7 groups (pyrovanadates) evince catalytic properties in the reactions of oxidative dehydrogenation of a series of organic compounds [1–5]. These vanadate phases belong to a small group of catalysts that enable the oxidation reaction to be directed towards the synthesis of desirable unsaturated compounds. Searching for new catalysts that will facilitate the course of this reaction with an even greater yield—is a topical and vital research problem. Considering these facts, it seems interesting to obtain such new components of potential catalysts that are products of reactions between the vanadates exhibiting catalytic properties. A physicochemical characterization of these new phases is of great value for determining the scope and limitations of the potential applications.

Results of investigations concerning the reactivity of iron(III) orthovanadate(V) towards the pyrovanadates(V) $M_2V_2O_7$ (M = Co, Mg, Zn) have shown the existence of a series of phases with the general formula $M_2FeV_3O_{11}$ [6–10]. These phases may prove to be interesting from the point of view of catalysis, which is due to the presence – among other things – of isolated VO_4 tetrahedra in their structure. A special interest has recently been attracted by the reactivity of $FeVO_4$ towards $Pb_2V_2O_7$. As a result of a reaction between these two vanadates exhibiting catalytic properties [3,5], not only a hitherto unknown compound of $Pb_2FeV_3O_{11}$ [11] has been obtained, but it has also been found during this research that still another unknown phase is formed within this system. However, as the investigations were conducted only in a limited concentration range of the system $FeVO_4$–$Pb_2V_2O_7$, the composition of the above phase has not been determined.

Thus the main aim of the present work was a determination of the composition of the new phase formed in the system $FeVO_4$–$Pb_2V_2O_7$ and a characterization of its selected physicochemical properties. Moreover, the determination of a phase diagram of the above system over the whole concentration range of its components has been planned. The acquired results have enabled establishing the temperature and component concentration ranges in which the new phase, as well as the phase previously discovered, $Pb_2FeV_3O_{11}$, exist [11].

2. Experimental

Reactants used in the research were $FeVO_4$ and $Pb_2V_2O_7$ obtained as a result of heating the stoichiometric mixtures of α-Fe_2O_3 (p.a., POCh, Poland) or $Pb(NO_3)_2$ (p.a., POCh, Poland) with V_2O_5 (p.a., Riedel-de Haën, Germany) in the following stages:

- synthesis of $FeVO_4$: $560\,^{\circ}C\,(20\,h) + 590\,^{\circ}C\,(20\,h) \times 2$;
- synthesis of $Pb_2V_2O_7$: $430\,^{\circ}C\,(20\,h) \times 2 + 600\,^{\circ}C\,(20\,h)$.

The syntheses were carried out by the conventional method of calcining samples [12,13]. The initial mixtures containing reacting substances were homogenized by grinding and heated in air for several stages until the composition of the samples did not change after two consecutive heating stages. After each heating stage the samples were gradually cooled down in furnace to room temperature, ground and

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Table 1
The composition of initial mixtures, their heating conditions and XRD analysis results of these samples after their last heating stage.

No.	Composition of initial mixtures (mol.%)		Heating conditions	Phases at equilibrium state
	$FeVO_4$	$Pb_2V_2O_7$		
1	10.00	90.00	570 °C (20 h) × 2	$Pb_2FeV_3O_{11}$, $Pb_2V_2O_7$
2	20.00	80.00		
3	30.00	70.00		
4	40.00	60.00		
5	45.00	55.00		
6	50.00	50.00		$Pb_2FeV_3O_{11}$
7	55.00	45.00	570 °C (20 h) × 3	$Pb_2FeV_3O_{11}$, $Pb_2Fe_2V_4O_{15}$
8	60.00	40.00		
9	63.00	37.00		
10	66.67	33.33		$Pb_2Fe_2V_4O_{15}$
11	71.00	29.00		$Pb_2Fe_2V_4O_{15}$, $FeVO_4$
12	75.00	25.00		
13	80.00	20.00		
14	85.00	15.00		
15	90.00	10.00		

examined by XRD method. The heating temperatures were chosen on the basis of DTA curves of selected samples.

The investigations by XRD method were carried out by means of an X-ray diffractometer HZG4/A2 (Carl Zeiss, Jena, Germany) and Ni-filtered Cu radiation. The identification of the phases occurring in the samples was conducted on the basis of their XRD characteristics contained in the PDF cards and in the work [11]. The powder diffraction pattern was indexed by means of the Dicvol program [14] (α-Al_2O_3 was used as the internal standard). The parameters of the unit cell were refined by the Refinement program of DHN/PDS package.

The measurements by DTA method were performed in air, in the temperature range 20–1000 °C, by means of the Paulik–Paulik–Erdey type derivatograph (MOM, Hungary). Samples of 500 mg were heated in quartz crucibles at a rate of 10 °C min^{-1}. The melting temperatures of the samples were taken as the onset temperatures of the first endothermic effects, recorded in their DTA curves. Accuracy of reading these temperatures amounted to ±5 °C (determined by repetitions).

The density of the new phase was determined by a method described in paper [15].

The IR spectrum of the new compound in the wavenumber range of 1400–250 cm^{-1} was obtained with the use of the spectrometer Specord M 80 (Carl Zeiss, Jena, Germany), applying the technique of peletting the sample with KBr at 1:300 weight ratio.

Selected samples were examined by means of an electron scanning microscope (JSM-1600, Jeol, Japan).

3. Results and discussion

15 mixtures of $FeVO_4$ and $Pb_2V_2O_7$ were prepared for the investigations. Their composition covering the whole component concentration range and their heating conditions are presented in Table 1. The compositions of samples 10 and 13 were chosen in such a way that they were lying at the points of intersection of the section $FeVO_4$–$Pb_2V_2O_7$ with two cross-sections of the ternary system PbO–V_2O_5–Fe_2O_3, *i.e.* with the sections PbV_2O_6–Fe_2O_3 and V_2O_5–$PbFe_2O_4$. The choice was made in this manner, because the compositions of phases forming in the ternary oxide systems correspond very often to the intersection points of the system's cross-sections. XRD analysis results for all samples obtained after the last heating stage (Table 1) allow the composition of the new phase formed in the system $FeVO_4$–$Pb_2V_2O_7$ to be established and the phase relations up to the solidus line in this system to be determined over the whole concentration range of the components.

In the concentration range of the reacting substances up to 50.00 mol.% $FeVO_4$ (in the initial mixtures) this compound reacts

Table 2
Indexing results for the $Pb_2Fe_2V_4O_{15}$ powder diffraction pattern.

No.	d_{obs} (nm)	d_{calc} (nm)	h	k	l	I (%)
1	1.1320	1.1296	1	0	0	27
2	0.5655	0.5648	2	0	0	6
3	0.5277	0.5273	0	1	0	12
4	0.5008	0.5004	1	−1	0	14
5	0.4720	0.4713	0	0	1	6
6	0.4582	0.4581	1	1	0	9
7	0.4402	0.4403	−2	0	1	12
8	0.4095	0.4096	2	−1	0	4
9	0.3912	0.3915	1	0	1	14
10	0.3767	0.3765	3	0	0	15
11	0.3652	0.3651	2	1	0	10
12	0.3572	0.3572	−3	0	1	7
13	0.3197	0.3196	−3	1	1	50
14	0.3157	0.3160	1	1	1	100
15	0.3128	0.3127	1	−1	1	48
16	0.2909	0.2910	3	1	0	12
17	0.2825	0.2824	4	0	0	68
18	0.2762	0.2765	−3	−1	1	21
19	0.2728	0.2729	2	−1	1	23
20	0.2635	0.2636	1	−2	0	29
21	0.2477	0.2476	−1	0	2	20
22	0.2355	0.2355	−2	1	2	8
23	0.2291	0.2290	2	2	0	14

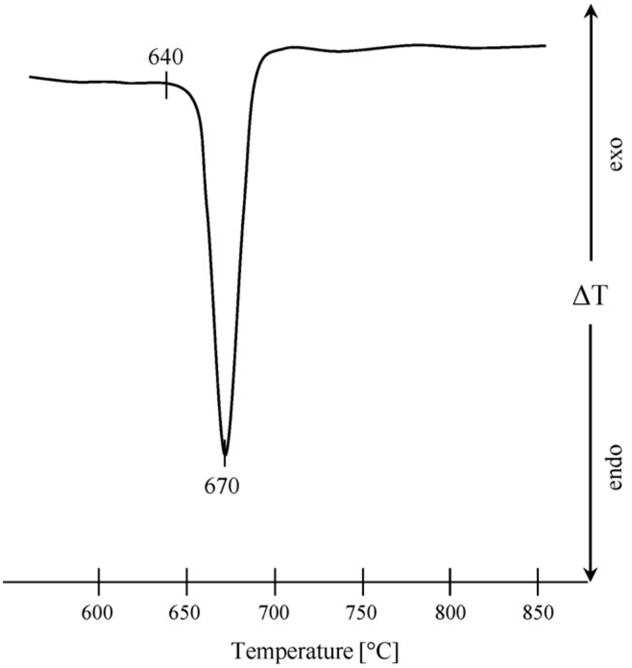

Fig. 1. Fragment of DTA curve of $Pb_2Fe_2V_4O_{15}$.

till completion with $Pb_2V_2O_7$ according to the equation [11]:

$$FeVO_{4(s)} + Pb_2V_2O_{7(s)} = Pb_2FeV_3O_{11(s)}$$

In this concentration range of the components of the investigated system, $Pb_2V_2O_7$ occurs in excess and coexists at equilibrium with $Pb_2FeV_3O_{11}$. A sample obtained through heating an equimolar mixture of $FeVO_4$ with $Pb_2V_2O_7$ is monophase and contains only $Pb_2FeV_3O_{11}$. In all remaining samples, *i.e.* above 50.00 mol.% $FeVO_4$ (in the initial mixtures), the presence of a hitherto unknown phase has been ascertained, only one of these samples being monophase. As a result of heating a mixture of the composition: 66.67 mol.% $FeVO_4$ and 33.33 mol.% $Pb_2V_2O_7$ (sample 10), a sample was obtained whose powder diffraction pattern consisted of a set of unidentified lines. In this sample no presence of the initial reacting substances or of any known phases formed in the system $PbO–V_2O_5–Fe_2O_3$ has been ascertained. Thus it has been concluded that the recorded set of reflections is by itself an XRD characteristics of a new compound, formed in solid state according to the equation:

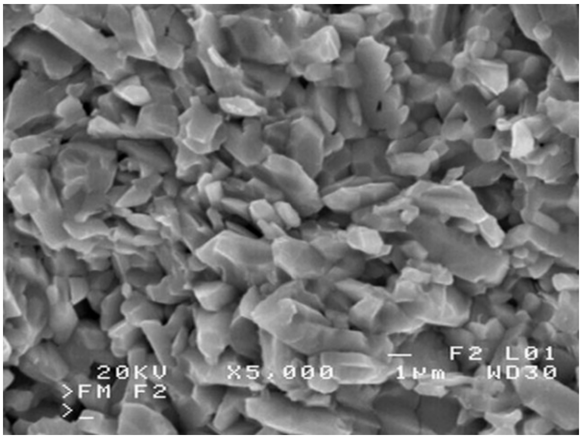

Fig. 2. SEM image of $Pb_2Fe_2V_4O_{15}$.

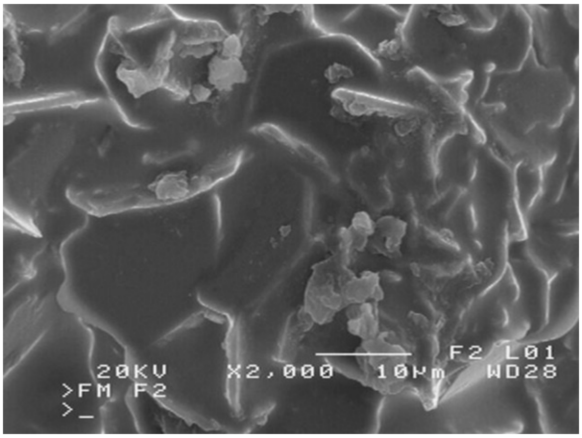

Fig. 3. SEM image of a sample of $Pb_2Fe_2V_4O_{15}$ heated for 3 h at 670 °C and rapidly quenched.

$$2FeVO_{4(s)} + Pb_2V_2O_{7(s)} = Pb_2Fe_2V_4O_{15(s)}$$

In the component concentration range of the investigated system from above 50.00 mol.% up to 66.67 mol.% $FeVO_4$ (in the initial mixtures), the new compound coexists at equilibrium with $Pb_2FeV_3O_{11}$. The samples that comprised over 66.67 mol.% $FeVO_4$ in their initial mixtures—in the state of equilibrium are also diphase and consist of mixtures of the new compound with iron(III) orthovanadate(V).

It is known from the literature information [16] that there exists a compound with the formula $Mn_2Fe_2V_4O_{15}$, *i.e.* with a composition analogous to the composition of the obtained new phase. However, some significant differences between the powder diffraction patterns of $Pb_2Fe_2V_4O_{15}$ and of $Mn_2Fe_2V_4O_{15}$ indicate that these phases are not isostructural.

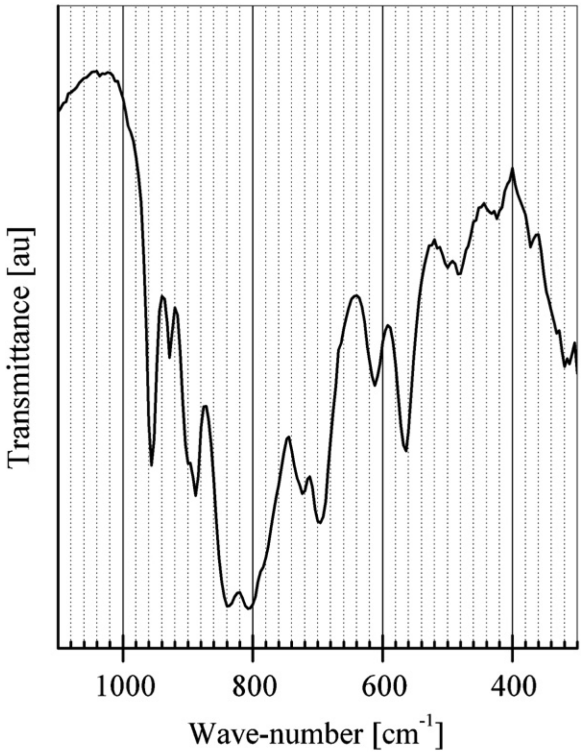

Fig. 4. IR spectrum of $Pb_2Fe_2V_4O_{15}$.

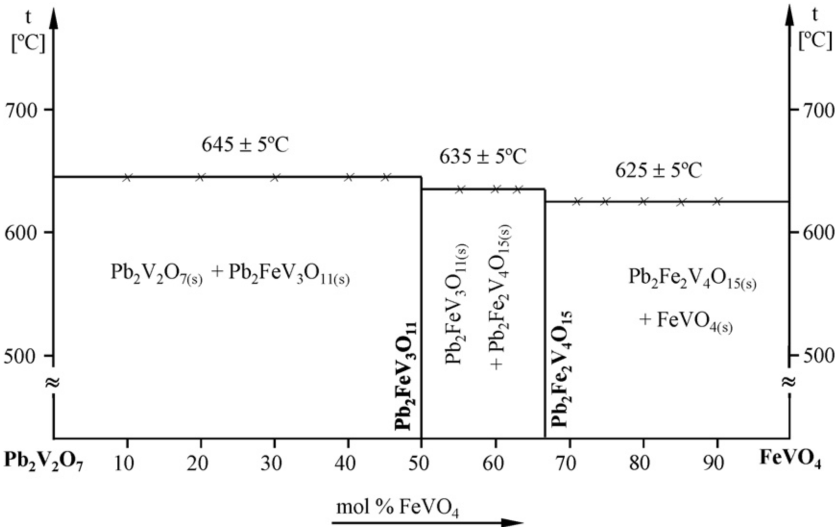

Fig. 5. Phase diagram up to the solidus line of the system $FeVO_4$–$Pb_2V_2O_7$.

In a further part of the work, some selected physicochemical properties of the new compound were investigated. $Pb_2Fe_2V_4O_{15}$ has a russetish orange sort of colour, and its density amounts to $d_{obs} = 5.30(5)\,g/cm^3$. The powder diffractogram of the new compound was subjected to indexing whose results are presented in Table 2. The obtained findings prove that $Pb_2Fe_2V_4O_{15}$ crystallizes in the triclinic system, its primitive unit cell parameters amounting to: $a = 1.2090(4)$ nm, $b = 0.5338(1)$ nm, $c = 0.5021(1)$ nm, $\alpha = 83.95(3)^\circ$, $\beta = 109.85(5)^\circ$, $\gamma = 98.24(3)^\circ$. The unit cell volume of $Pb_2Fe_2V_4O_{15}$ is equal to $V = 0.3011\,nm^3$, and the number of stoichiometric units per unit cell $Z = 1$. The XRD calculated density of the new compound amounts to $5.35\,g/cm^3$.

Fig. 1 presents a fragment of a DTA curve of the compound $Pb_2Fe_2V_4O_{15}$. In this curve only one endothermic effect was recorded with its onset temperature equal to 640 ± 5 °C. In order to determine the type of the transformation that this effect is due to, a sample of the investigated compound was heated additionally for 3 h at 670 °C, *i.e.* at the temperature of the maximum of this effect, and next the sample was rapidly cooled to room temperature and subjected to an XRD analysis. The obtained results have shown that the only crystalline phase present in the investigated sample is iron(III) oxide. At the moment of taking the sample outside of the furnace at 670 °C, the sample was molten. Thus it can be concluded that the thermal effect beginning at 640 ± 5 °C is due to an incongruent melting of the new compound with a deposition of one solid phase, *i.e.* Fe_2O_3.

The acquired findings about the way of the melting of $Pb_2Fe_2V_4O_{15}$ have been corroborated by SEM investigations. Fig. 2 presents a SEM image of $Pb_2Fe_2V_4O_{15}$. In order to show more clearly the shapes of the crystals of the new compound, the image is presented in a magnification of 5000×. Fig. 3 shows an image of the same $Pb_2Fe_2V_4O_{15}$ sample heated additionally at 670 °C for 3 h and next rapidly cooled down. Against a background of an amorphous phase, fine crystals are visible resembling as to their morphology the Fe_2O_3 crystals whose SEM image has been shown in an earlier work [11].

Fig. 4 presents an IR spectrum of the new phase. According to the literature information, the absorption bands recorded in the wavenumber range 990–640 cm^{-1} can be most likely ascribed to stretching vibrations of V–O bonds within VO_4 tetrahedra [17–20]. In this wavenumber range, some bands caused by stretching vibrations of M–O bonds within MO_5 polyhedra (M = Fe, V) can also occur [18,19]. The absorption bands registered in the remaining wavenumber range, *i.e.* 640–300 cm^{-1}, can be associated with bending vibrations of O–V–O bonds [17–20] and with vibrations of M–O bonds within the polyhedra PbO_x [21,22] and FeO_6 [18,19]. The presence of an acute and intense band with its maximum at 955 cm^{-1} as well as of an acute band at 925 cm^{-1} evidences a very strong deformation of the polyhedra present in the structure.

On the ground of the XRD (Table 1) and DTA results for all samples after attaining equilibrium, a phase diagram has been elaborated up to the solidus line of the system in which the new phase $Pb_2Fe_2V_4O_{15}$ is formed. The temperatures of the solidus line were determined in such a way that they were based on the onset temperatures of first endothermic effects recorded in the DTA curves of samples at an equilibrium state. The presented diagram (Fig. 5) comprises all the acquired information about the ranges of temperature and the component concentrations for which the compounds $Pb_2Fe_2V_4O_{15}$ and $Pb_2FeV_3O_{11}$ exist in the system $FeVO_4$–$Pb_2V_2O_7$.

4. Conclusion

1. A new compound with the formula $Pb_2Fe_2V_4O_{15}$ has been obtained as a result of a reaction between $FeVO_4$ and $Pb_2V_2O_7$ at a molar ratio equal to 2:1.
2. $Pb_2Fe_2V_4O_{15}$ crystallizes in the triclinic system.
3. The new compound melts incongruently at 640 ± 5 °C with a deposition of solid Fe_2O_3.
4. In the system $FeVO_4$–$Pb_2V_2O_7$ in the solid state form two phases: $Pb_2Fe_2V_4O_{15}$ and $Pb_2FeV_3O_{11}$.

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