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Study of the system $FePO_4$–$FeVO_4$ prepared from the solution

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The samples of the pseudobinary system $(FePO_4)_{1-x}$–$(FeVO_4)_x$ with $x = 0$–1 were prepared by precipitation from a solution of iron nitrate and ammonium phosphate/vanadate, and the evolution of their structure during the heating of the precipitate within the temperature range of 20–1000 °C was studied by thermal analysis, X-ray diffraction and infrared spectroscopy. The samples dried at 120 °C were amorphous having a high specific surface area of 160–222 $m^2 g^{-1}$ and their crystallization took place at 440–560 °C. The regions of solid solutions between the two boundary phases were smaller than 10 mol % of the second phase and a new crystalline phase was formed in the system at the composition of $FePO_4$:$FeVO_4$ = 1:1.

1. Introduction

Iron phosphates and iron vanadates are amongst the compounds which have a catalytic activity in various industrially important reactions, such as the oxidation of isobutyric acid to methacrylic acid [1]. Iron orthophosphate, $FePO_4$, is unique among the crystalline iron phosphates, owing to its structure which is analogous to silica, having iron and phosphorus tetrahedrally coordinated with oxygen [2]. In the other phosphates, the iron atom has coordination numbers of 5 and 6 [3]. First studies of the $FePO_4$ crystal structure were made in 1936 [4], when Cagliotti found that $FePO_4$ is isomorphous with berlinite, $AlPO_4$, and with α-SiO_2. Its pseudotetragonal elementary unit cell has lattice constants of $a = 0.5035$ nm and $b = 0.5588$ nm. The refinement of the crystal structure was published by Ng and Calvo [5].

Iron vanadate was revealed as a compound during a study of the phase diagram of Fe_2O_3–V_2O_5 by Burdese [6]. According to this diagram, the compound $FeVO_4$ melts incongruently at 840 °C. Its structure was studied by Robertson and Kostiner [7] who found that it belongs to the triclinic crystal group and its elementary unit cell has the parameters $a = 0.6719$ nm, $b = 0.8060$ nm, $c = 0.9254$ nm, $\alpha = 96.65°$, $\beta = 106.57°$, $\gamma = 101.60°$ with $Z = 6$. In this structure, three independent iron atoms (two in distorted octahedral and one in a distorted trigonal bipyramidal environment of oxygen atoms) are joined to create a doubly bent chain of six edge-sharing polyhedra. The chains are joined by VO_4^{3-} tetrahedra. The room-temperature Mössbauer spectrum exhibits six resonance lines of an essentially equal area. Because each of the three iron atoms lies in a distorted polyhedron of oxygen atoms, Robertson and Kostiner [7] assumed that these six lines represent a set of three resonance absorptions, each a quadrupole-split doublet. The doublet with the large quadrupole splitting (1.113 $mm\,s^{-1}$) and a lower isomer shift (+0.582 $mm\,s^{-1}$) was ascribed to the five-coordinated Fe^{3+} ion, and the other two doublets with close values of isomer shift (0.664 and 0.667 $mm\,s^{-1}$) to the six-coordinate Fe^{3+} ions.

The infrared spectrum of $FeVO_4$ was investigated by Baran and Botto [8]. Four groups of vibrational bands were observed in this spectrum: (a) the group around 950 cm^{-1} ascribed to the stretching vibrations of VO_4 groups, (b) the group between 600 and 700 cm^{-1}, (c) the group around 500 cm^{-1} ascribed to the stretching vibrations of Fe–O coordination polyhedra, and (d) the vibrational bands under 400 cm^{-1} having a more complex origin (bending vibrations and mixed-type vibrations).

In the present work, materials of the system $FePO_4$–$FeVO_4$ prepared from the solution of iron nitrate by the precipitation, were studied. This method enables these materials to be prepared in a very fine form, with a high value of specific surface area. Attempts were made to investigate the process of their annealing and to identify the phases formed by the heat treatment of the products.

2. Experimental procedure

The samples of the system $(FePO_4)_{1-x}$–$(FeVO_4)_x$ were prepared within the whole concentration region of $x = 0$–1 with steps of 10 mol %, according to the following procedure. Aqueous solutions of ammonium hydrogenphosphate, $(NH_4)_2HPO_4$, and ammonium vanadate, NH_4VO_3, in a given stoichiometric ratio, were added to the solution of $Fe(NO_3)_3 \cdot 9H_2O$. The obtained suspension was

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neutralized with ammonia solution (1 : 1) and the beige precipitate was decanted three times, filtered and then dried 24 h at 120 °C.

The prepared samples were investigated by thermal analysis using the thermogravimetric (TG) method (Derivatograph, Budapest) and differential thermal analysis method (DTA) (Perkin–Elmer DTA 1700) in the temperature region 20–1000 °C with Al_2O_3 as a reference material at a scan rate of $10\,°\mathrm{C\,min^{-1}}$. X-ray diffraction measurements of the samples annealed at 700 °C for 24 h were carried out on the DRON diffractometer with $\mathrm{Co}K_\alpha$ radiation. Infrared spectra were studied in the infrared spectrometer, Perkin–Elmer model 684, with the sample powders dispersed in nujol mulls.

The composition of the samples was checked by X-ray spectral analysis using the EDAX system mounted on the SEM microscope Tesla BS 301.

The surface area of the samples was measured with a surface area analyser (Micromeritics 2200A).

3. Results and discussion

The samples obtained by precipitation and dried at 120 °C were amorphous, as determined by X-ray diffraction. The analysis of the products showed that the molar ratio Fe: (P + V) ranged from 1.00–1.15, i.e. there is a slight overstoichiometric surplus of the metal in the studied system.

All the prepared samples possessed high values of specific surface area ranging from 160–222 $\mathrm{m^2\,g^{-1}}$ in the samples dried at 120 °C. With increasing heat-treatment temperature of the samples, the value of the surface area decreased rapidly as seen in Table I for three samples of the system

3.1. Thermal analysis

Thermogravimetric analysis of the samples within the region 20–600 °C showed that the water contained in the dried samples escaped gradually during heating in two consecutive steps in the region 60–400 °C. The loss of water (16–17.5 wt %) is accompanied by two broad endothermic peaks on the DTA curve (see Fig. 1) situated in the region of 60–250 °C and 250–400 °C. This decrease corresponds to about 1.6–1.8 mol H_2O, or 1 mol $FePO_4$ or $FeVO_4$ respectively. The course of the dehydration shows that the water in the samples is predominantly chemisorbed due to a high value of the surface area of the dried product.

TABLE I Changes in the values of the specific surface area of the samples of $(FePO_4)_{1-x}$–$(FeVO_4)_x$ system after heating the samples for 2 h at 200–800 °C

Annealing temperature (°C)	Specific surface area ($\mathrm{m^2g^{-1}}$)		
	$FePO_4$	$FePO_4$–$FeVO_4$	$FeVO_4$
120	210.0	221.6	162.4
200	151.6	214.0	74.9
400	109.6	118.7	54.9
600	10.9	8.8	10.9
800	1.4	0.2	0.5

The results of the differential thermal analysis (Figs 1 and 2) revealed an exothermic peak on the DTA curves on heating for all the samples; in samples containing 0–50 mol % $FeVO_4$, the peak was in the region around 560 °C; in the samples with 60–100 mol % $FeVO_4$, the peak position shifted to lower temperatures with increasing content of $FeVO_4$ up to 440 °C (Fig. 3). This peak was assigned to the crystallization of the amorphous product. This assignment was supported by XRD experiments carried out below and above the mentioned temperature, and confirmed by repeating DTA, which showed no peak in this region in the product heated above the mentioned temperature.

In the samples with 30–60 mol % $FeVO_4$, during heating there is a broad endothermic peak in the DTA curves with the onset at ~770 °C. This enthalpic change (denoted T_2 in Table II) is reversible, and on cooling the DTA curve exhibits an endothermic peak positioned at a slightly lower temperature. The shape of this band and its steady position could be explained as a eutectic transformation. This effect is accompanied by sintering of the sample, which could be caused by the formation of a liquid phase.

Another endothermic effect (denoted T_3 in Table II), but sharper and at a higher temperature of 840 °C, can be seen in the DTA curves during heating of the samples with 70–90 mol % $FeVO_4$. This effect is also reversible, and on cooling there is a corresponding

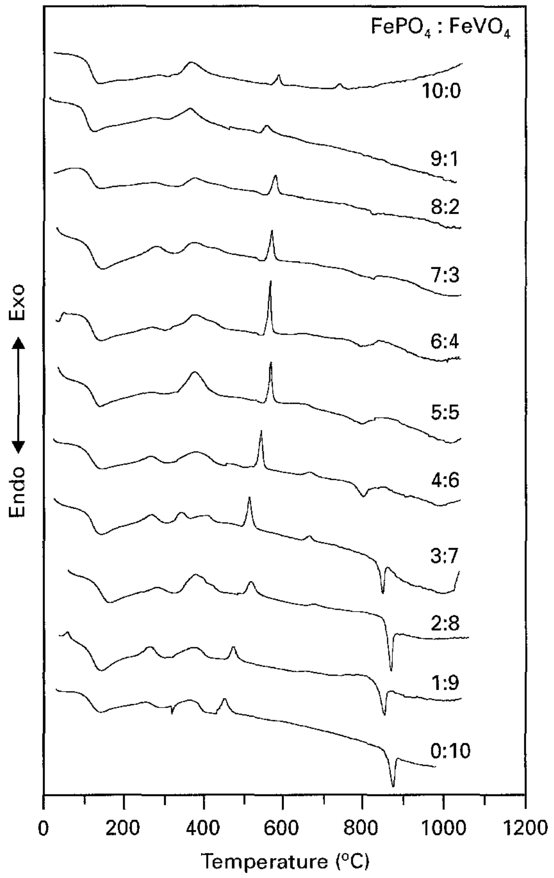

Figure 1 DTA curves of the thermal analysis (on heating) of samples from the $FePO_4$–$FeVO_4$ system.

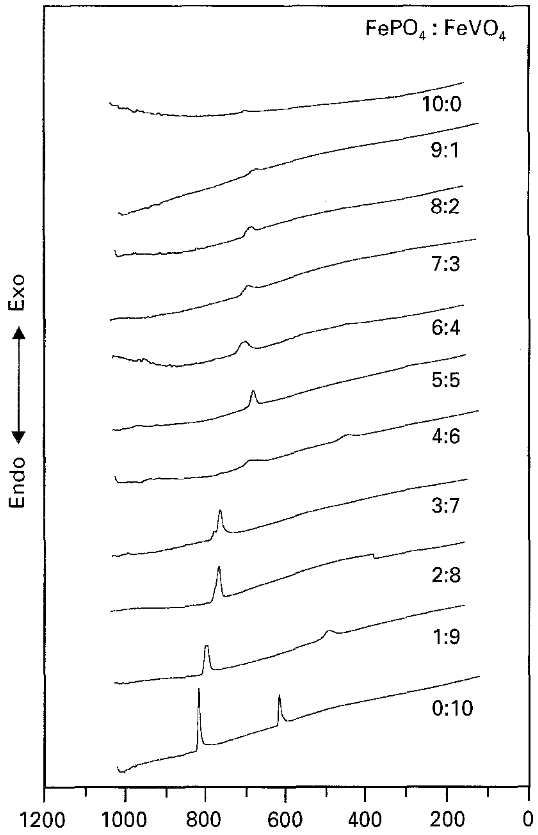

Figure 2 DTA curves of the thermal analysis (on cooling) of samples from the $FePO_4$–$FeVO_4$ system.

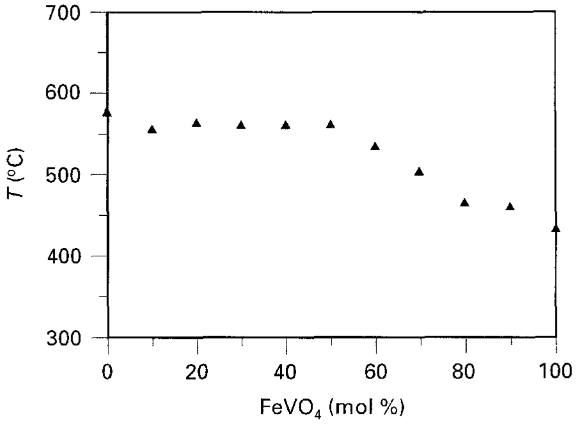

Figure 3 Crystallization temperatures of samples from the $FePO_4$–$FeVO_4$ system.

exothermic peak lying on the DTA curves at temperatures lower, by about 60 °C, in comparison to the position of the effect on heating. This effect is also ascribed to eutectic change, peaking at about 80 mol % $FeVO_4$. The onset temperatures of the observed peaks on the DTA curves are summarized in Table II.

TABLE II Changes of crystallization temperatures of samples $(FePO_4)_{1-x}$–$(FeVO_4)_x$ system

$FePO_4$ (mol %)	Heating[a]			Cooling[a]
	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)
0	576			703
10	555			697
20	563			696
30	560	764		695
40	560	781		717
50	560	763		684
60	533	775		702
70	502		839	766
80	463		835	769
90	458		838	799
100	431		863	815

[a] T_1–T_4, onset temperatures of enthalpic peaks on DTA curves.
T_1, crystallization temperature.
T_2, T_3, eutectic temperature.
T_4 exothermic peaks on cooling corresponding to T_2 and T_3.

3.2. X-ray diffraction

X-ray diffraction measurements revealed that the samples of $FePO_4$–$FeVO_4$ obtained by precipitation and drying at 120 °C were amorphous and only those samples heated above their corresponding crystallization temperature, revealed diffraction lines. Therefore, for the phase analysis, the samples were annealed at 700 °C for 24 h, to obtain a better crystallinity. The obtained X-ray diffraction patterns are shown in Fig. 4a and b. The X-ray diffraction patterns revealed that the solid solutions on both sides of the system are limited to less than 10 mol % second phase, because in the samples of $9FePO_4$–$1FeVO_4$ and $1FePO_4$–$9FeVO_4$, new diffraction lines were observed. As can be seen from the diffraction data, a new crystalline phase with a composition of about $5FePO_4$–$5FeVO_4$ is formed in the studied system. This new phase has a diffraction pattern which cannot be obtained by superposition of the diffraction lines of the compounds of $FePO_4$ and $FeVO_4$. Such a result was supposed to take place, because the structures of both mother phases, $FePO_4$ and $FeVO_4$, are different.

3.3. Infrared spectra

The samples of the $FePO_4$–$FeVO_4$ system after drying at 120 °C revealed a few broad bands. Only after heat treatment of the samples to 700 °C, were sharper bands observed in the infrared spectra. The obtained IR spectra of six samples of the system are shown in Fig. 5.

The dominant bands in the high-frequency region of 800–1300 cm^{-1} belong to the stretching vibrations of the anionic part of the samples, i.e. to PO_4 and VO_4 tetrahedral units, respectively. The higher frequency part (1000–1300 cm^{-1}) can be ascribed to the stretching vibrations of PO_4 units; the lower-frequency part (800–1000 cm^{-1}) can be ascribed to the stretching vibrations of VO_4 units. The shapes of the bands are broader than in compounds with an ionic structure, due to the coupling of basic structural units into a structural network. This coupling is very strong, especially for $FePO_4$ having SiO_2-type structure. An observable decrease in the strength of the bands belonging to PO_4 units can be seen in the IR spectra of samples with 70–90 mol % $FeVO_4$, with the originally

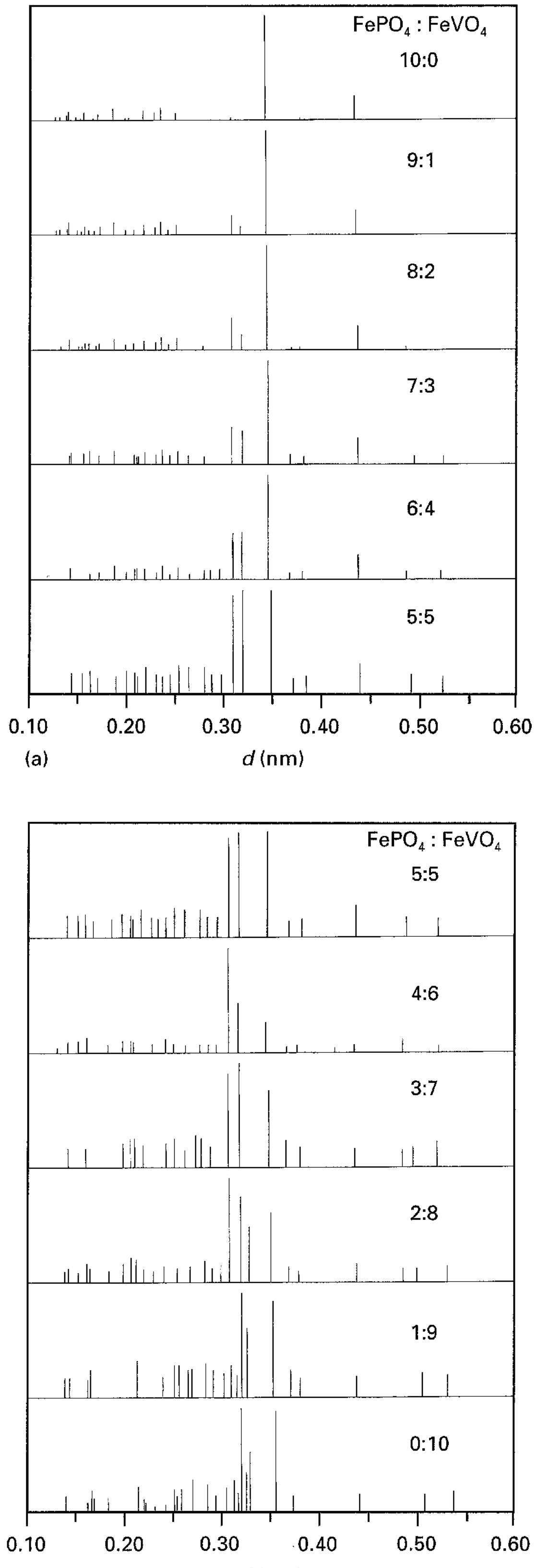

Figure 4 (a, b) X-ray diffraction patterns of the $FePO_4$–$FeVO_4$ system heat treated at 700 °C.

broad band split into the three bands of 1058, 1085 and 1133 cm^{-1}. In these samples the vibrational band belonging to the stretching vibrations of VO_4 units is split into a band at 853 cm^{-1} and close bands of 914 and 960 cm^{-1}.

In the spectral region of 500–800 cm^{-1} we can observe vibrational bands which can be assigned to the vibrations of FeO_x polyhedra. In the infrared spectra of the samples with a high $FePO_4$ content there are two bands at 588 and 636 cm^{-1}. The strength of these two bands decreases with decreasing $FePO_4$ content. Therefore, we assigned these bands tentatively to the vibrations of FeO_4 tetrahedra, which are specific for the $FePO_4$ structure. On the other hand, in samples with a high $FeVO_4$ content in the mentioned region, two groups of vibrational bands were observed at 515 cm^{-1} and 630–730 cm^{-1}. According to Baran and Botto [8] the vibrational bands of FeO_6 groups lie in the region of 550–410 cm^{-1}, while those of FeO_5 lie at higher frequencies. Therefore, we ascribed the band at 515 cm^{-1} in the IR spectra of $FePO_4$–$FeVO_4$ samples with a high $FeVO_4$ content to the vibrations of FeO_6 octahedra. The vibrational bands around 690 cm^{-1} were assigned to the vibrations of FeO_5 structural groups which are also present in the $FeVO_4$ structure [7]. The vibrational bands corresponding to the FeO_x polyhedra are not clearly resolvable in the infrared spectra of samples with the composition of $x = 0.4$–0.6. Infrared spectra of the samples with an intermediate structure reveal generally broader bands and are not so clearly separated as in the pure compounds.

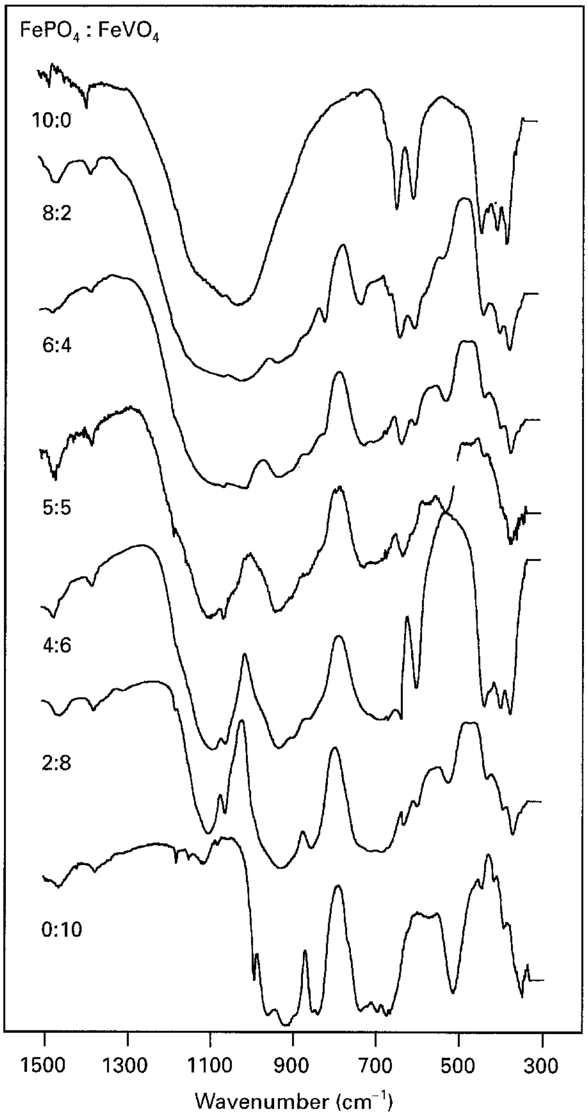

Figure 5 IR absorption spectra of the $FePO_4$–$FeVO_4$ samples heat treated at 700 °C.

Vibrational bands observed in the IR spectra of the $(FePO_4)_{1-x}$–$(FeVO_4)_x$ samples under 500 cm^{-1} can be assigned to the skeletal deformational vibrations of the structural network and their assignment to polycrystalline materials is tedious.

4. Conclusion

The study of the samples of $FePO_4$–$FeVO_4$ prepared by precipitation from solution showed that the samples dried at 120 °C are amorphous and possess a high specific surface area. After annealing above 500–600 °C they become crystalline. A new crystalline phase is formed in the system at the composition of $FePO_4:FeVO_4 = 1:1$. The observed molar ratio of Fe: $(P + V) = 1.0$–1.15 could be due to a partial hydrolysis of the product during the decantation of the precipitate, when iron can form hydroxide which converts, after annealing, to the iron oxide, because slight amounts of Fe_2O_3 were detected in some samples with the application of Mössbauer spectroscopy.

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