

SYNTHESIS AND SELECTED PROPERTIES OF $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$

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Abstract

A new compound $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ has been obtained by solid state reaction. Temperature of its incongruent melting amounts to $890 \pm 5^\circ\text{C}$. Results of indexing the powder diffraction pattern and unit cell parameters of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ are also given. This compound is probably isostructural with $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ (where $M = \text{Zn, Mg, Mn}$). IR spectrum of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ phase is presented.

Keywords: $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, DTA, IR, XRD

Introduction

It is known from literature that orthovanadates(V) of divalent and trivalent metals as well as divanadates(V) of divalent metals catalyse oxidation processes of various organic compounds [1–5]. Catalytic activity of these phases is associated with the presence in their structure of isolated VO_4 tetrahedra (orthovanadates) or V_2O_7 groupings, arising from a linkage between two tetrahedra (divanadates). It can be expected that also compounds being formed as a result of reactions between the above mentioned vanadates will possess interesting properties from the point of view of catalysis.

During our earlier investigations on the reactivity of FeVO_4 towards divanadates $\text{M}_2\text{V}_2\text{O}_7$ (where $M = \text{Zn, Mg, Co}$) we obtained a series of new compounds belonging to the family $\text{M}_2\text{FeV}_3\text{O}_{11}$ [6–8]. The compounds $\text{Zn}_2\text{FeV}_3\text{O}_{11}$ and $\text{Mg}_2\text{FeV}_3\text{O}_{11}$ are isostructural and in their structure isolated tetrahedra VO_4 can be distinguished [9]. The compound $\text{Co}_2\text{FeV}_3\text{O}_{11}$ occurs in two polymorphic modifications [8]. Results of our research indicate that the low-temperature polymorph $\alpha\text{-Co}_2\text{FeV}_3\text{O}_{11}$ is probably isostructural with $\text{Zn}_2\text{FeV}_3\text{O}_{11}$ and $\text{Mg}_2\text{FeV}_3\text{O}_{11}$ [8]. Moreover, in our other works we have pointed out that as a result of reactions between FeVO_4 and orthovanadates $\text{M}_3\text{V}_2\text{O}_8$ (where $M = \text{Zn, Mg, Co}$) some new compounds are also formed, belonging to other family $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [10, 11]. Selected physicochemical properties of two from among them, *i.e.* $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ and $\text{Mg}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, we have presented in the work [10]. Results of our investigations im-

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ply that $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ and $\text{Mg}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ are isostructural with $\text{Mn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [10]. In the structure of $\text{Mn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ the isolated tetrahedra VO_4 also occur [12] beside the FeO_6 , MnO_6 and MnO_5 polyhedra.

The aim of this work was a closer characterisation of the third compound from among those belonging to the family $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, *i.e.* $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$.

Experimental

The synthesis of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ was performed by using the following reacting substances: CoCO_3 (95%, Fluka Chemie, Switzerland), V_2O_5 (p.a., Riedel-de Haën, Germany), Fe_2O_3 (p.a., POCh, Poland) and also FeVO_4 and $\text{Co}_3\text{V}_2\text{O}_8$. The compounds FeVO_4 , $\text{Co}_3\text{V}_2\text{O}_8$ and the $\text{Co}_4\text{Fe}_{3.33}\text{V}_6\text{O}_{24}$ phase were obtained as a result of heating appropriate stoichiometric mixtures of Fe_2O_3 , V_2O_5 and CoCO_3 in the following stages:

- synthesis of FeVO_4 : $560^\circ\text{C}(20\text{ h}) + 590^\circ\text{C}(20\text{ h})\times 2$
- synthesis of $\text{Co}_3\text{V}_2\text{O}_8$: $560^\circ\text{C}(20\text{ h}) + 590^\circ\text{C}(20\text{ h})\times 2 + 650^\circ\text{C}(20\text{ h})$
- synthesis of $\text{Co}_4\text{Fe}_{3.33}\text{V}_6\text{O}_{24}$: $560^\circ\text{C}(20\text{ h}) + 720^\circ\text{C}(20\text{ h})\times 2$

The reactions were carried out by the conventional method of calcining samples. Appropriate portions of reacting substances were ground in order to homogenise them and next, after shaping them into pellets, they were heated in the atmosphere of air in several stages. On completion of each heating stage the samples were gradually cooled in furnace to ambient temperature, ground and examined by XRD method, some selected preparations also by DTA. Results of investigations by XRD and DTA methods allow a determination of composition of samples and an establishing of their melting temperatures [13–15]. After shaping the samples again into pellets they were subjected to further heating. This procedure was repeated until monophase samples were obtained.

The DTA investigations were conducted in air in quartz crucibles, using the Paulik–Paulik–Erdey type derivatograph (MOM, Hungary). The measurements were carried out in the atmosphere of air, in the temperature range $20\text{--}1000^\circ\text{C}$, at a heating rate of $10^\circ\text{C min}^{-1}$. The mass of a sample amounted to 500 mg. The accuracy of reading the thermal effects temperatures recorded in DTA curves, as established on the base of repetitions, was equal to $\pm 5^\circ\text{C}$.

The density of the compound $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ was determined by applying the method of hydrostatic weighting in CCl_4 , described in the work [16].

The powder diffraction patterns of the samples were received by using the X-ray diffractometer DRON-3 (Bourestnik, Sankt Petersburg, Russia), applying a cobalt tube ($\text{CoK}\alpha$) as a source of radiation, equipped with an iron filter. Identification of phases present in the samples was performed on the base of X-ray characteristics contained in the PDF cards [17] and data reported in the works [12, 18].

The powder diffraction pattern of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ was indexed by means of the program Refinement from the package DHN/PDS, using $\alpha\text{-SiO}_2$ as an internal standard for accurate determination of diffraction lines positions.

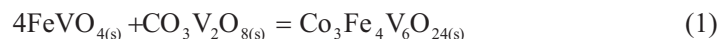
The IR spectrum of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, in the wave-number range of $1400\text{--}250\text{ cm}^{-1}$, was obtained with the use of the spectrometer Specord M 80 (Carl Zeiss, Jena, Germany), applying the technique of pressing pellets with KBr at a mass ratio 1:300.

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

Results and discussion

In order to find out whether any new compound belonging to the family $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ is formed as a result of a solid state reaction between FeVO_4 and $\text{Co}_3\text{V}_2\text{O}_8$, a mixture of the composition: 80 mol% FeVO_4 and 20 mol% $\text{Co}_3\text{V}_2\text{O}_8$ was prepared. This mixture, corresponding to $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ by its composition, was heated at 680°C for 20 h and next at 780°C for 20 h.

Analysis by XRD method of a sample obtained after the last heating cycle did not show any presence of reactants or other known compounds formed in the system $\text{CoO}\text{--}\text{V}_2\text{O}_5\text{--}\text{Fe}_2\text{O}_3$. The X-ray diffraction pattern of this sample revealed only a set of diffraction lines the positions of which differed slightly from the positions of diffraction lines characteristic for the $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ type compounds (where $M = \text{Zn}, \text{Mg}, \text{Mn}$) [10, 12]. Thus it was concluded that the set of these lines was characteristic of a new compound $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ that was obtained as a result of a solid state reaction occurring in accordance with the equation:



The $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ compound was also obtained according to the reaction:



by heating a stoichiometric mixture of reacting substances in the following stages: $560^\circ\text{C}(20\text{ h}) + 580^\circ\text{C}(20\text{ h}) + 740^\circ\text{C}(20\text{ h}) + 780^\circ\text{C}(20\text{ h})$.

The compound $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ is dark brown in colour. Its density amounts to $3.92(5)\text{ g cm}^{-3}$. SEM image of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ is presented in Fig. 1.

The melting temperature of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, read from the DTA curve (Fig. 2) as the onset of first endothermic effect, is equal to $890 \pm 5^\circ\text{C}$.

Results of XRD analysis showed for the compound $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, molten at 920°C and next rapidly cooled to ambient temperature, that it melts incongruently with a separation of a solid phase the diffraction pattern of which resembles much the diffractograms of lyonsite-type phases, *i.e.* $\text{Co}_4\text{Fe}_{3.33}\text{V}_6\text{O}_{24}$ and $\text{Co}_{3.6}\text{Fe}_{3.6}\text{V}_6\text{O}_{24}$ [12, 18]. These diffractograms were calculated on the base of the structural data of these phases [12, 18]. The other endothermic effect recorded in the DTA curve of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ is due to crossing the liquidus line. The way of melting is corroborated by the results of SEM investigations. The SEM image of a $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ sample 'frozen' at 920°C (Fig. 3) reveals crystals distinctly differing by morphology from the $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ crystals (Fig. 1), but resembling very much the crystals of $\text{Co}_4\text{Fe}_{3.33}\text{V}_6\text{O}_{24}$ (lyonsite) (Fig. 4). Table 1 presents results of indexing the powder diffraction pattern of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$.

Table 1 Results of indexing the powder diffraction pattern of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$

No.	d_{obs}/nm					d_{obs}/nm					No.	d_{obs}/nm					$I/\%$
	1	2	3	4	5	1	2	3	4	5		1	2	3	4	5	
1	0.7366	0.7377	0.7377	0	1	0	20	11	0.3268	0.3271	-2	0	1	28			
2	0.6940	0.6934	0.6934	0	-1	1	15	12	0.3201	0.3199	2	-1	0	10			
3	0.6171	0.6164	0.6164	1	0	0	10	13	0.3137	0.3137	1	0	2	55			
4	0.4857	0.4853	0.4853	-1	1	1	9	14	0.3060	0.3060	0	2	1	100			
5	0.4645	0.4642	0.4642	1	-1	1	10	15	0.3000	0.3002	-1	-2	2	5			
6	0.4440	0.4437	0.4437	0	0	2	10	16	0.2884	0.2886	-2	1	2	11			
7	0.3902	0.3903	0.3903	0	-2	1	5	17	0.2830	0.2832	2	-1	1	6			
8	0.3684	0.3678	0.3678	1	-2	0	25	18	0.2802	0.2801	-2	-1	1	8			
9	0.3465	0.3467	0.3467	0	-2	2	6	19	0.2768	0.2765	-2	-1	2	8			
10	0.3403	0.3400	0.3400	1	-1	2	8	20	0.2649	0.2649	2	0	1	15			

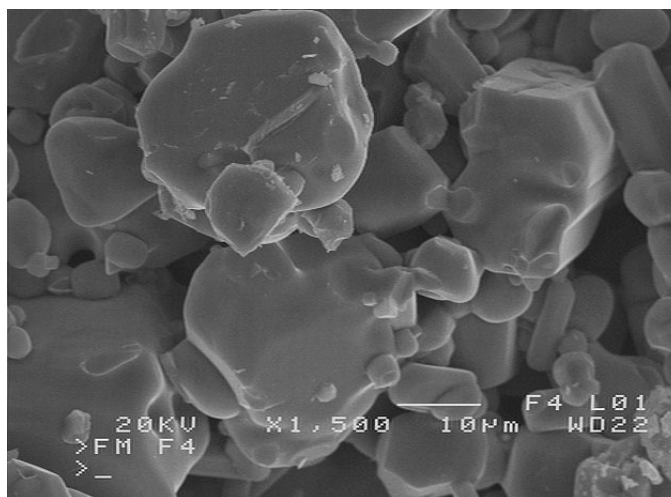


Fig. 1 SEM image of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$

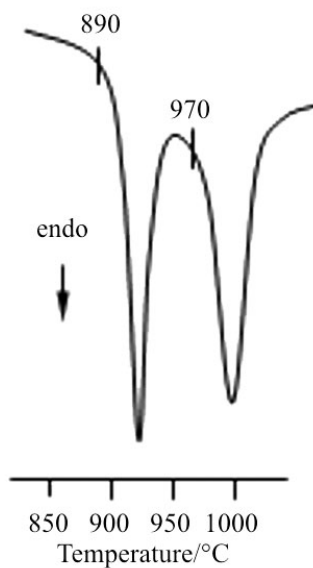


Fig. 2 DTA curve of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$

$\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ crystallises in the triclinic system; the unit cell is primitive; the number of stoichiometric units per unit cell $Z = 1$; the unit cell parameters amount to: $a = 0.6685(2)$ nm, $b = 0.8003(5)$ nm, $c = 0.9764(8)$ nm, $\alpha = 105.30(9)^\circ$, $\beta = 105.21(6)^\circ$, $\gamma = 101.83(7)^\circ$. The unit cell volume is equal to $V = 0.4646$ nm³, XRD calculated density $d_{\text{rig}} = 3.89$ g cm⁻³. A close similarity both between the X-ray pow-

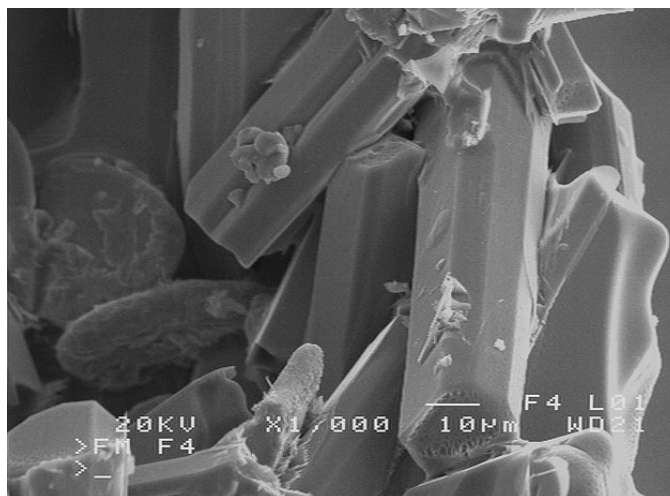


Fig. 3 SEM image of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ 'frozen' at 920°C

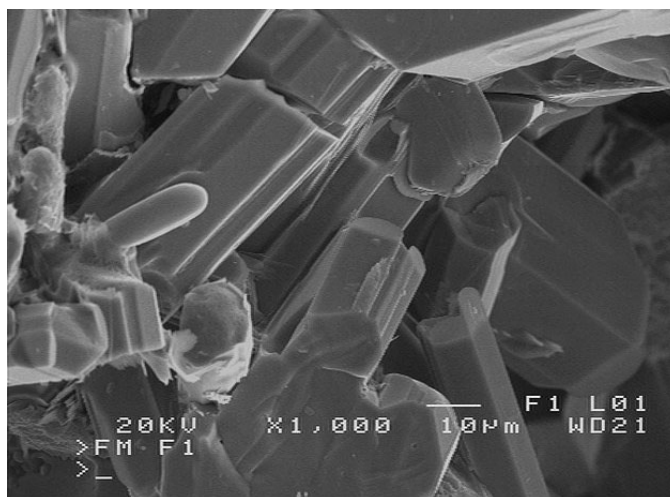


Fig. 4 SEM image of $\text{Co}_4\text{Fe}_{3.33}\text{V}_6\text{O}_{24}$

der diffraction patterns and between the corresponding unit cell parameters of the compounds $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ and $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ (where $M = \text{Zn}, \text{Mg}, \text{Mn}$) [10, 12] indicates that all these phases are most probably isostructural. The IR spectrum of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ is presented in Fig. 5.

The IR spectrum of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ consists of three broad absorption bands lying in the wavenumber ranges $1060\text{--}850$, $850\text{--}\sim 620$, $\sim 620\text{--}250\text{ cm}^{-1}$. In the structure of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ the presence of coordination polyhedra occurring in the structure of

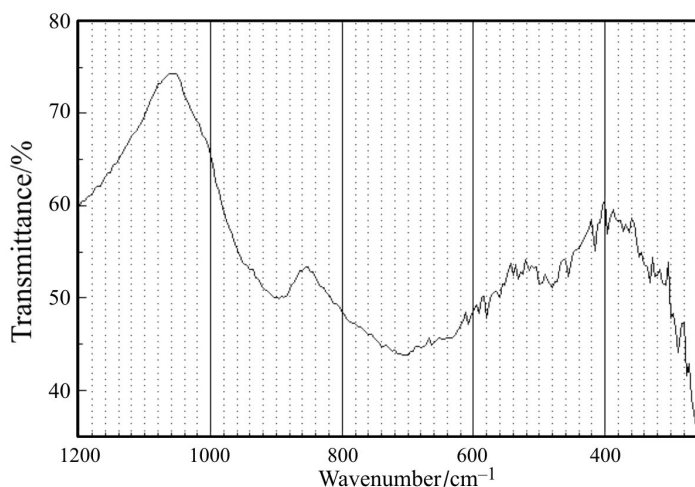


Fig. 5 IR spectrum of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$

$\text{Mn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [12] can be expected. The bands with their maxima at about 900 and 710 cm^{-1} correspond probably to stretching vibrations of the V–O bonds in the VO_4 tetrahedra [19–22]. The absorption bands occurring in the remaining range of wavenumbers, *i.e.* $\sim 620\text{--}250\text{ cm}^{-1}$ can be ascribed to stretching vibrations of the Fe–O and Co–O bonds in the FeO_6 , CoO_6 and CoO_5 polyhedra as well as to bending vibrations of the O–V–O bonds in the VO_4 tetrahedra [19–23].

Conclusions

- A new compound $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ belonging to a recently discovered family of compounds has been obtained as a result of solid state reactions according to the reactions (1) and (2).
- The temperature of incongruent melting of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ amounts to $890\pm 5^\circ\text{C}$.
- This compound crystallises in the triclinic system.
- A close similarity both between the powder diffraction patterns and between the corresponding unit cell parameters of $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ and $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ (where $M = \text{Zn}, \text{Mg}, \text{Mn}$) indicates that these compounds are probably isostructural.

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