REACTIVITY OF $FeVO_4$ TOWARDS $MgMoO_4$ IN THE SOLID-STATE

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Abstract

A compound of the formula $Fe_3Mg_2Mo_2V_3O_{20}$ has been obtained as a result of a reaction between $FeVO_4$ and $MgMoO_4$ taken at a molar ratio of 3:2. This compound crystallises in the monoclinic system and its unit cell parameters are the following: a=0.6971 nm, b=0.9055 nm, c=1.2542 nm, γ=102.00°, Z=2.

Keywords: DTA, $FeVO_4$, IR, $MgMoO_4$, molybdatovanadate, XRD

Introduction

Mixed-metal oxides play an important role in many areas of physics, chemistry and materials science [1–6]. The combination two or more metals in an oxide matrix can produce materials with novel interesting physicochemical properties. That can lead to using these new materials in technological applications.

It is known from literature reports that molybdates(VI) and vanadates(V) of divalent and trivalent metals which contain isolated VO_4 or MoO_4 tetrahedra have promising catalytic properties in the process of oxidative dehydrogenation of light alkanes [3, 7–9].

Unlike the well-known properties of molybdates(VI) and vanadates(V) of divalent and trivalent metals in the structure of which isolated tetrahedra Mo/V–O_4 occur, only few molybdato(VI)vanadates(V) are known at all. Namely, in the recent decade a family of molybdato(VI)vanadates(V) of divalent metals with the formula $M_{2.5}VMoO_8$, where M=Mn, Mg, Co, Zn [8–11], has been obtained and thoroughly investigated. Moreover, in the system Fe_2O_3–V_2O_5–MoO_3 there exist two compounds, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ [14–17], and a substitutional solid solution of MoO_3 in $Fe_2V_4O_{13}$ with a limited solubility [18–20], whereas in analogous systems containing chromium or aluminum instead of iron the compounds $CrVMoO_7$ and $AlVMoO_7$ are formed [21, 22]. The structure and properties of $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ are known and have been described in many articles [23–25]. It is also known that $FeVMoO_7$ forms solid solutions with $CrVMoO_7$ and $AlVMoO_7$ [26, 27]. Molybdatovanadates of $Fe_{4-x}Cr_xV_2Mo_3O_{20}$ type, where x is from 1 to 2, are also known [28].

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The solid solution formed in the system Fe$_2$O$_3$–V$_2$O$_5$–MoO$_3$ results from an incorporation of Mo^{6+} ions into the sites of V^{5+} ions in the crystal lattice of Fe$_2$V$_4$O$_{13}$. In the above mentioned system this phase crystallizes along the line Fe$_2$V$_4$O$_{13}$–FeVMoO$_7$ [17, 19, 20], however the literature information on how the compensation of excessive charge introduced into the Fe$_2$V$_4$O$_3$ lattice by the Mo^{6+} ions occurs – is contradictory. From one side, it has been proven by Mössbauer spectroscopy that the excessive positive charge is compensated by a reduction of an amount of Fe^{3+} ions, equivalent with respect to Mo^{6+}, to Fe^{2+} ions [20]. Thus the substitution mechanism of Mo^{6+} for V^{5+} is described by the formula Fe$^{3+}_{2-x}$Fe$^{2+}_x$V$_{4-x}$Mo$_x$O$_{13}$, where $0<x\leq0.6$ [20]. On the other hand, Wang *et al.* have reported that the overall charge is balanced by introduced oxygen atoms accompanying the substitution of Mo^{6+} for V^{5+}. These authors have presented the substitution mechanism of Mo^{6+} for V^{5+} by the formula Fe$_2$V$_{4-x}$Mo$_x$O$_{13+x/2}$ indicating that the substitution causes no reduction of either V^{5+} or Mo^{6+} ions, however they do not comment at all on the oxidation state of iron in the formed phase [29].

Recently, new solid solution crystals of (Mg$_{1-x}$Fe$_x$)(Mo$_{2-x}$V$_x$)O$_7$ ($0.13\leq x\leq0.47$) have been obtained which are formed in the quaternary MgO–Fe$_2$O$_3$–V$_2$O$_5$–MoO$_3$ system on the FeVMoO$_7$–MgMo$_2$O$_7$ tie line [30].

The aim of the work was investigating whether on another tie line, namely FeVO$_4$–MgMoO$_4$, of the quaternary system Fe$_2$O$_3$–MgO–V$_2$O$_5$–MoO$_3$, any other hitherto unknown molybdato(VI)vanadates(V) with mixed cation are formed.

Experimental

The initial reagents used for preparation of phases needed in the syntheses were: Fe$_2$O$_3$ (a.p., POCh), V$_2$O$_5$ (a.p., Riedel–de Haën), 3MgCO$_3$·Mg(OH)$_2$·H$_2$O (a.p., POCh) and MoO$_3$ (a.p., POCh). From these reagents the phases FeVO$_4$, MgMoO$_4$, Mg$_3$V$_2$O$_8$ and Fe$_2$(MoO$_4$)$_3$ were obtained as a result of heating the stoichiometric mixtures of suitable compounds in the following conditions:

- FeVO$_4$:   550°C(24 h)+600°C(24 h)+600°C(24 h)
- MgMoO$_4$:   550°C(24 h)+650°C(24 h)+700°C(24 h)
- Mg$_3$V$_2$O$_8$:   550°C(24 h)+650°C(24 h)+700°C(24 h)
- Fe$_2$(MoO$_4$)$_3$:   650°C(24 h)+700°C(24 h)+700°C(24 h)

Reacting substances, i.e. FeVO$_4$ and MgMoO$_4$, weighed in appropriate portions were always homogenised by grinding and shaped into pellets. The pellets were placed in porcelain crucibles and heated in the atmosphere of air. On each heating stage the samples were gradually cooled to ambient temperature, ground and subjected to DTA investigations and their contents determination by XRD method. After shaping them into pellets again they were heated further. This procedure was repeated until samples in equilibrium state were received.

The DTA investigations were performed by means of a derivatograph (MOM, Hungary). Samples of 1000 mg by mass were placed in quartz crucibles. All measurements were conducted in the atmosphere of air, in the temperature range 20–1000°C, at a heating rate of 10° min^{-1}.

Phases occurring in the samples were identified on the base of an X-ray phase analysis performed with the use of the diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia). The source of radiation was a cobalt tube (CoK$_\alpha$) with an iron filter, angular range was 12–52° 2θ with step size 0.02° 2θ and counting time per step 10 s. The identification of phases was conducted by comparison with the XRD characteristics contained in the PDF cards [31].

Unit cell parameters were determined by applying the program Powder [32, 33]. For indexing – 30 diffraction lines were selected the positions of which were read from a diffraction pattern recorded for a sample with internal standard KCl (space group Fm3m; $a=b=c=0.629$ nm).

The density was determined by the method described in the work [34].

IR spectra were recorded in the wave-number range 1100–250 cm^{-1} by means of the spectrometer Specord M80 (Carl Zeiss, Jena, Germany). The technique of pressing pellets with KBr at a mass ratio of 1:300 was applied.

Results and discussion

In order to investigate the solid-state reaction occurring between FeVO$_4$ and MgMoO$_4$, five mixtures were prepared from separately obtained FeVO$_4$ and MgMoO$_4$. Table 1 presents the composition of initial mixtures, their heating conditions and XRD analysis results after the final heating stage. The research results compiled in Table 1 prove that FeVO$_4$ and MgMoO$_4$ are not inert towards each other, but react in the solid-state. In the diffraction patterns of samples containing in their initial mixtures up to 60 mol% FeVO$_4$ a set of diffraction lines characteristic for MgMoO$_4$ was recorded together with another set of lines that could not possibly be ascribed to any phases known to be formed in the quaternary system Fe$_2$O$_3$–MgO–V$_2$O$_5$–MoO$_3$. This latter set of lines was denoted as LX. Figure 1 presents the powder diffraction pattern of the sample contain-
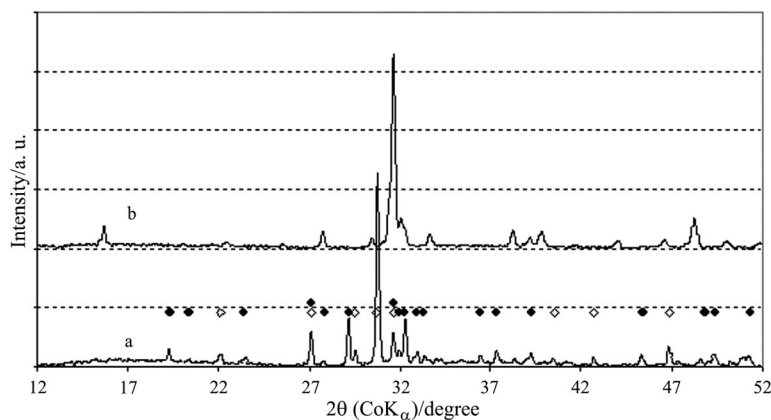
Fig. 1 Powder diffraction patterns of a – MgMoO$_4$+FeVO$_4$ mixture and of
b – Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$, where $\diamond$ – MgMoO$_4$, $\bullet$ – FeVO$_4$ and the non-marked
lines in curve b all belong to Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$

Table 1 Initial mixtures composition, their heating conditions and XRD analysis results of the samples after the last heating stage

No.	Composition of initial mixtures/mol%	Heating conditions/°C	Phases at equilibrium
1	60MgMoO$_4$+40FeVO$_4$	600	MgMoO$_4$+FeVO$_4$
		650	MgMoO$_4$+LX*
		700	LX*+MgMoO$_4$
2	50MgMoO$_4$+50FeVO$_4$	600	MgMoO$_4$+FeVO$_4$+LX$^*_{(tr.)}$
		650	MgMoO$_4$+LX*
		700	LX*+MgMoO$_4$
3	42.8MgMoO$_4$+57.2FeVO$_4$	600	MgMoO$_4$+FeVO$_4$+LX$^*_{(tr.)}$
		650	MgMoO$_4$+LX*
		700	LX*+MgMoO$_4$
4	40MgMoO$_4$+60FeVO$_4$	600	MgMoO$_4$+FeVO$_4$+LX$^*_{(tr.)}$
		650	MgMoO$_{4(tr.)}$+FeVO$_{4(tr.)}$+LX*
		700	LX*
5	33.3MgMoO$_4$+66.7FeVO$_4$	600	MgMoO$_4$+FeVO$_4$+LX$^*_{(tr.)}$
		650	LX*+FeVO$_4$
		700	LX*+FeVO$_4$

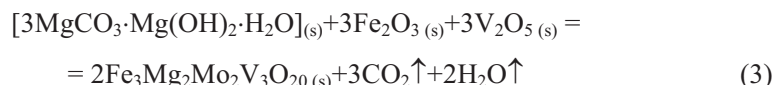LX* – new compound; $_{(tr.)}$ – traces

ing 40 mol% MgMoO$_4$ and 60 mol% FeVO$_4$ after the final heating stage (curve b) and in their initial mixture (curve a). The diffraction pattern of a sample containing 60 mol% FeVO$_4$ in its initial mixture contained only the LX set of lines. On the diffractogram of the last listed sample beside the LX set some lines characteristic for FeVO$_4$ were registered.

The obtained results indicate that the solid-state reaction between iron(III) orthovanadate(V) and magnesium molybdate(VI) leads to a formation of a new compound, which can be expressed by the equation:

$$2MgMoO_{4\,(s)}+3FeVO_{4\,(s)} = Fe_3Mg_2Mo_2V_3O_{20\,(s)} \tag{1}$$

The compound Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$ was also obtained as a product of a solid-state reaction occurring among Fe$_2$(MoO$_4$)$_3$, Mg$_3$V$_2$O$_8$ and FeVO$_4$ mixed at a molar ratio of

2:2:5 or among 3MgCO$_3$·Mg(OH)$_2$·H$_2$O, MoO$_3$, Fe$_2$O$_3$ and V$_2$O$_5$ heated in the same conditions as the sample No. 4. The reactions taking place can be written in a form:

$$2Mg_3V_2O_{8\,(s)}+2Fe_2(MoO_4)_{3\,(s)}+5FeVO_{4\,(s)} = 3Fe_3Mg_2Mo_2V_3O_{20\,(s)} \qquad (2)$$

$$[3MgCO_3·Mg(OH)_2·H_2O]_{(s)}+3Fe_2O_{3\,(s)}+3V_2O_{5\,(s)} =$$

$$= 2Fe_3Mg_2Mo_2V_3O_{20\,(s)}+3CO_2\uparrow+2H_2O\uparrow \qquad (3)$$

The products of the reactions (1), (2) and (3) were subjected to chemical analysis and their densities were determined. The chemical analysis showed that the mean content of metallic elements in the investigated samples amounted to 18.3 mass% Fe, 5.8 mass% Mg, 21.5 mass% Mo, 17.8 mass% V, which can be compared to the values calculated on the base of the assumed formula: 19.02 mass% Fe, 5.52 mass% Mg, 17.35 mass% V, 21.78 mass% Mo. The density of Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$ is equal to 3.79 g cm^{-3}. The compound Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$ is honey yellow. Its melting temperature read from the DTA curve (Fig. 2) as the beginning of endothermic effect amounts to 850±5°C. The XRD analysis results of Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$ molten at 890°C and next rapidly quenched to ambient temperature proved that this compound melts congruently.
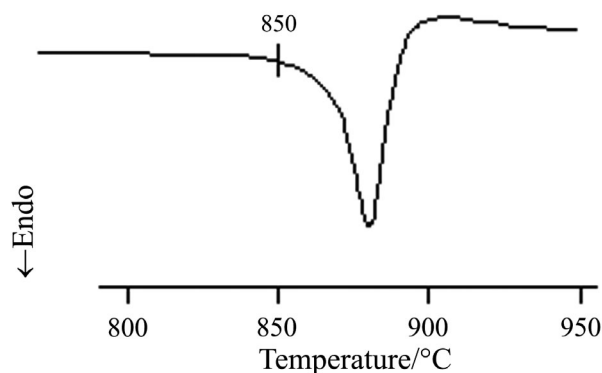

Fig. 2 DTA curve of Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$

Results of indexing the powder diffraction pattern of Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$ are presented in Table 2. The compound Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$ crystallises in the monoclinic system, a primitive unit cell with the following parameters: a=0.6971 nm, b=0.9055 nm, c=1.2542 nm, β=102.00°. The unit cell volume is V=774.4 nm^3. The number of stoichiometric units per unit cell Z=2 and the density amounts to $d_{calc.}$=3.78 g cm^{-3}.

Figure 3 presents IR spectra of the compound Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$ (curve b) and of the physical mixture of magnesium molybdate(VI) with iron(III) orthovanadate(V) at a molar ratio of 2:3 (curve a) – for comparison. The oscillation spectrum of Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$ is definitely less complex than the spectrum of the components mixture from which Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$ was obtained. In the diagram of Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$ four regions of absorption bands can be distinctly distinguished. Namely, the first one exhibiting two maxima at 975 and 928 cm^{-1} can be ascribed with great probability to

Table 2 Results of indexing the powder diffraction pattern of Fe$_3$Mg$_2$Mo$_2$V$_3$O$_{20}$

No.	d_{exp}/nm	d_{cal}/nm	$h\,k\,l$	I/I_0 /%
1	0.6565	0.6571	1 1 0	14.0
2	0.4778	0.4778	1 1 1	2.5
3	0.4605	0.4605 0.4614	0 2 1 1 2 0	3.2
4	0.3766	0.3738	2 0 1	10.9
5	0.3411	0.3413	2 1 1	7.0
6	0.3282	0.3281	2 2 0	100.0
7	0.3243	0.3243	1 0 2	17.6
8	0.3093	0.3092	1 3 1	13.9
9	0.2733	0.2734	2 3 0	11.1
10	0.2672	0.2672	3 –3 0	6.7
11	0.2641	0.2641	1 –3 2	6.0
12	0.2629	0.2630	2 –2 2	9.3
13	0.2388	0.2389 0.2390	2 2 2 3 –4 0	2.8
14	0.2264	0.2263 0.2261	4 –1 0 3 –4 1	4.7
15	0.2252	0.2253	3 0 2	4.3
16	0.2190	0.2191 0.2187	1 1 3 3 3 0	16.0
17	0.2116	0.2115	3 –5 0	4.8
18	0.2076	0.2075	1 2 3	
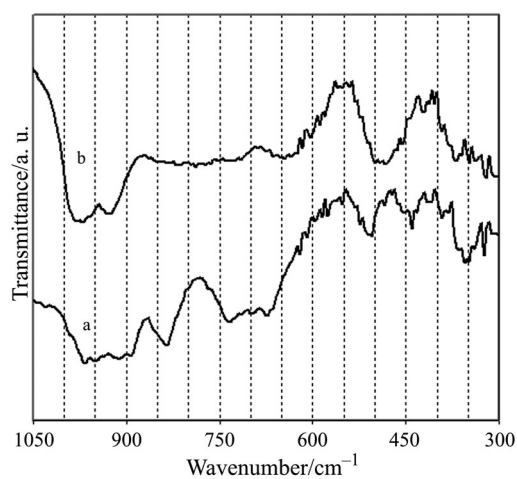
Fig. 3 IR spectra of a – initial mixture and b – Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$

stretching vibrations of M-O bonds in the tetrahedra VO$_4$ and MoO$_4$ [35, 36]. The second small band with its maximum at 650 cm^{-1} can be associated with stretching vibrations of bridging bonds M–O–M [37, 38] and the next band with a broad maximum at 490 cm^{-1} is certainly due to stretching vibrations of the bonds Fe–O and Mg–O in the polyhedra FeO$_6$, MgO$_6$ and MgO$_5$ [38]. The last region of absorption bands lying at 400–250 cm^{-1} possesses several maxima caused probably by bending vibrations of M–O bonds in the tetrahedra VO$_4$ or MoO$_4$ [35, 38].

Conclusions

The presented research results allow the following conclusions to be drawn:

- In the solid-state, FeVO$_4$ and MgMoO$_4$ are not inert towards each other, but enter into reaction at a molar ratio of 3:2 with a formation of a hitherto not described in literature phase Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$. This compound can also be obtained according to Eqs (2) and (3).
- The compound Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$ melts congruently at 850±5°C.
- The compound Mg$_2$Fe$_3$Mo$_2$V$_3$O$_{20}$ crystallises in the monoclinic system and its unit cell parameters are the following: a=0.6971 nm, b=0.9055 nm, c=1.2542 nm, β=102.00°.

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