

PHASE FORMATION IN THE $\text{FeVO}_4\text{--Co}_3\text{V}_2\text{O}_8$ SYSTEM

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Phase relations in the solid state in the $\text{FeVO}_4\text{--Co}_3\text{V}_2\text{O}_8$ system, in the whole range of components concentration have been studied. It was found that the composition of the phase of the howardevansite type structure, formed in the investigated system, corresponds with the $\text{Co}_{2.616}\text{Fe}_{4.256}\text{V}_6\text{O}_{24}$ formula. The phase of the lyonsite type structure has a homogeneity range with the $\text{Co}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$ formula ($0.476 < x < 1.667$). The melting temperature and the volume of the unit cell of the lyonsite type structure phase increases together with the rise of cobalt quantity contained in it. Basing on the results of the DTA and XRD measurements a phase diagram of the $\text{FeVO}_4\text{--Co}_3\text{V}_2\text{O}_8$ system up to the solidus line was constructed.

Keywords: $\text{Co}_{2.616}\text{Fe}_{4.256}\text{V}_6\text{O}_{24}$, DTA, howardevansite type phase, lyonsite type phase, XRD

Introduction

Double vanadate $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ forms two polymorphic modifications. The $\alpha\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ modification is the mineral lyonsite, which was discovered in the summit crater fumaroles of the Izalco volcano (El Salvador) [1]. This vanadate, when synthesized in the laboratory, crystallizes in a different form that is as $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$, with a structure closely related to mineral howardevansite $\text{NaCuFe}_2\text{V}_3\text{O}_{12}$ [2]. The phase with the lyonsite type structure is formed in laboratory conditions as well, however its composition differs significantly from the corresponding $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ compound [3]. Belik *et al.* claims [3] that the composition of synthetic $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ also deviates from the stoichiometric one. However, both phases, the α - and β -, have ranges of homogeneity [3].

The studies on the systems where phases of the lyonsite or howardevansite type structure are formed are interesting, not only because of the peculiarity of their behaviour but also due to the presence of isolated VO_4 tetrahedrons in their structure [1, 2]. Such tetrahedrons, building a crystal lattice of orthovanadates(V) of divalent metals, are undoubtedly connected with their catalytic activity in the reactions of the oxidizing dehydrogenation of the saturated to unsaturated compounds [4, 5]. Therefore, one can presume that similar characteristics may occur in the case of the phases of the lyonsite and howardevansite type structures.

With this assumption in mind, the $\text{FeVO}_4\text{--Co}_3\text{V}_2\text{O}_8$ system seems to be an interesting object of investigation. The results of our re-

search [6, 7] as well as the literature reports [8, 9] indicate that in this system both the phase of the lyonsite as well as the howardevansite type structure crystallizes. However, the range of homogeneity of both phases still has not been determined.

In this work the phase formation in the $\text{FeVO}_4\text{--Co}_3\text{V}_2\text{O}_8$ system in the whole range of components concentration has been reported. Determining the range of homogeneity of the phases of the lyonsite and howardevansite type structures was the main point of the work.

Experimental

24 mixtures of FeVO_4 and $\text{Co}_3\text{V}_2\text{O}_8$ were prepared for the investigations. The reactions were performed with a conventional sintering method [10, 11]. The appropriate portions of reacting substances were homogenized and after shaping them into pellets, were heated in the atmosphere of air for several stages until the state of equilibrium was obtained. The heating temperatures were selected on the basis of the DTA curves of the chosen samples and also on the basis of the results of the previous investigations [7, 12]. At each heating stage the samples were gradually cooled down in the furnace to ambient temperature and, after grinding, they were examined by the XRD method, whereas some other selected samples by the DTA as well. When the composition of the samples did not change after two consecutive heating stages, it was assumed that the state of equilibrium in the samples was obtained.

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Table 1 The composition of the initial mixtures, the heating conditions and the results of XRD analysis of the samples obtained after final heating stage

No.	Composition of initial mixtures/mol%		Heating conditions	Phases detected
	FeVO ₄	Co ₃ V ₂ O ₈		
1	96.00	4.00		
2	93.33	6.67	680°C(20 h) +780°C(20 h)·2	FeVO ₄ , H-type phase
3	85.72	14.28		
4	84.00	16.00		
5	83.00	17.00		
6	82.00	18.00		H-type phase
7	81.00	19.00		
8	80.00	20.00	680°C(20 h) +780°C(20 h) +840°C(20 h)·2	H-type phase, L-type phase
9	78.00	22.00		
10	76.00	24.00		
11	75.00	25.00		
12	74.00	26.00		L-type phase, H-type phase*
13	73.00	27.00		
14	71.43	28.57		
15	66.67	33.33		L-type phase
16	58.43	41.57		
17	57.00	43.00		
18	56.00	44.00	680°C(20 h) + 780°C(20 h) + 920°C(20 h)·2	L-type phase, Co ₃ V ₂ O ₈ *
19	54.00	46.00		
20	50.00	50.00		
21	40.00	60.00		
22	30.00	70.00		L-type phase, Co ₃ V ₂ O ₈
23	20.00	80.00		
24	10.00	90.00		

*amount on the verge of detection by XRD method

Diffraction patterns were obtained using the DRON –3 X-ray diffractometer (Bourestnik, Sank Petersburg, Russia) and Fe-filtered Co radiation. The identification of the phases was conducted on the basis of the XRD characteristics [13] contained in the PDF cards [14] and the data presented in works [8, 9]. The powder diffraction patterns were indexed by means of the Refinement program of DHN/PDS package, using α -Al₂O₃ as the internal standard.

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

Results and discussion

Table 1 presents the compositions of the initial mixtures, the heating conditions and the results of the XRD analysis of the samples after the last stage of heating. The compositions of samples were selected in such a way that they encompassed the whole range of the studied system components' concentrations. High concentration of the samples in the ranges 14.28–28.57 and 41.57–46.00% mol Co₃V₂O₈ (in the initial mixtures) was to facilitate establishing the range of homogeneity of the phases with the lyonsite and howardevansite type structure. From the data presented in the table it follows that the components of the FeVO₄–Co₃V₂O₈ system react one with another, forming the phase with the lyonsite and the phase with howardevansite type structure (hereafter the L- and H-type phase).

The results of the analysis conducted by means of the XRD method, performed after each heating stage indicate that the L-type phase forms in the first stage of reaction already, that is at the temperature of 680°C , what is more this phase was identified in all samples. After the second stage of heating, i.e. at 780°C , in samples 1–12, the presence of the H-type phase was noted. This phase occurred in some of those samples already at the temperature of 680°C , but its amount was very slight. Thus it can be assumed that the synthesis of the H-type phase requires higher temperature than that one of the L-type phase. The compositions of samples at equilibrium are presented in Table 1.

The samples which contain in the initial mixtures up to 16.00 mol% $\text{Co}_3\text{V}_2\text{O}_8$, in the state of equilibrium comprise the mixture of iron(III) orthovanadate(V) and the H-type phase. The sample having the initial composition of 17.00 mol% $\text{Co}_3\text{V}_2\text{O}_8$ and 83.00 mol% FeVO_4 is monophasic in the state of equilibrium and contains only the H-type phase. In the next samples at equilibrium the L-type phase appears. The H-type and L-type phases co-exist at equilibrium in the range of concentrations from 18.00 to 26.00 mol% $\text{Co}_3\text{V}_2\text{O}_8$ in the initial mixtures. In the samples containing (in initial mixtures) 27.00, 28.57, 33.33, 41.57 and 43.00 mol% $\text{Co}_3\text{V}_2\text{O}_8$ at equilibrium only one phase was identified, that is the L-type phase. In the remaining range of concentrations this phase co-exists at equilibrium with cobalt(II) orthovanadate(V).

The presented results prove that the L-type phase has a wide range of homogeneity. The change of composition of this phase can be described as $\text{Co}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$ ($0.476 < x < 1.667$) where $x=0.476$ corresponds with the sample with the content of 26.00 mol% $\text{Co}_3\text{V}_2\text{O}_8$ (sample 12), and $x=1.667$ with the one of 44.00 mol% $\text{Co}_3\text{V}_2\text{O}_8$ (sample 18) in the initial mixtures. When sample 12 remains at equilibrium, the presence of the H-type phase is still recorded with the XRD method, however its quantity is on the verge of detection. The additionally conducted detection tests lead to a conclusion that the XRD method allows to state the presence of the H-type phase in the mixture with the L-type phase where the content of the H-type phase is about 2.00 mol%. Similarly, in the state of equilibrium the presence of $\text{Co}_3\text{V}_2\text{O}_8$ is still recorded in sample 18 with the help

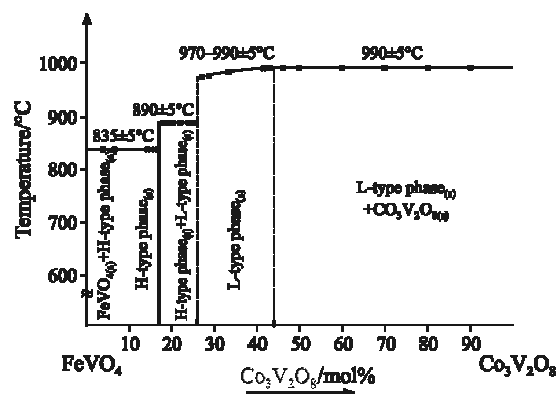


Fig. 1 The phase diagram of the system $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$ up to the solidus line

of the XRD method, although its amount is on the verge of detection. The conducted detection tests indicate that the presence of $\text{Co}_3\text{V}_2\text{O}_8$ in the mixture with the L-type phase can be stated with the XRD method, when it contains about 5 mol% $\text{Co}_3\text{V}_2\text{O}_8$.

The compositions of monophasic samples where only the L-type phase was identified, can be noted as $\text{Co}_{3.827}\text{Fe}_{3.449}\text{V}_6\text{O}_{24}$ (sample 13), $\text{Co}_4\text{Fe}_{3.333}\text{V}_6\text{O}_{24}$ (sample 14), $\text{Co}_{4.5}\text{Fe}_3\text{V}_6\text{O}_{24}$ (sample 15), $\text{Co}_{5.286}\text{Fe}_{2.476}\text{V}_6\text{O}_{24}$ (sample 16) and $\text{Co}_{5.412}\text{Fe}_{2.392}\text{V}_6\text{O}_{24}$ (sample 17), which in the $\text{Co}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$ formula corresponds with $x=0.551$; 0.667; 1; 1.524; 1.608.

Moreover, the results presented in Table 1 indicate that contrary to the L-type phase, the H-type phase which is formed in the $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$ system does not have the homogeneity range. The composition of the monophasic sample where only the H-type phase was identified (sample 5), corresponds with the $\text{Co}_{2.616}\text{Fe}_{4.256}\text{V}_6\text{O}_{24}$ formula, which can be also noted as $\text{Co}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$ where $x=-0.256$. Thus the composition of this phase varies from the $\text{Co}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ proposed earlier [7] and is significantly different from the composition of the phases with the howardite type structure, which we obtained and studied in similar systems, i.e. $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ and $\text{Mg}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [15–17].

On the basis of the DTA curves and the XRD analysis results for the samples at equilibrium the phase diagram of the $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$ system in the subsolidus area was constructed [18] (Fig. 1). The solidus line temperatures were determined on the basis of the onset temperatures of the first endother-

Table 2 The composition of the phase with the lyonsite type structure and its unit cell volumes

No.	The composition of L-type phase	The unit cell parameters/nm			The unit cell volume/nm ³
14	$\text{Co}_4\text{Fe}_{3.333}\text{V}_6\text{O}_{24}$	$a=0.4965(1)$	$b=1.0221(2)$	$c=1.7215(4)$	0.8737
15	$\text{Co}_{4.5}\text{Fe}_3\text{V}_6\text{O}_{24}$	$a=0.4977(2)$	$b=1.0219(2)$	$c=1.7208(4)$	0.8753
16	$\text{Co}_{5.286}\text{Fe}_{2.476}\text{V}_6\text{O}_{24}$	$a=0.5012(1)$	$b=1.0201(1)$	$c=1.7184(2)$	0.8785

mic effects recorded in the DTA curves of the corresponding samples. The homogeneity range of the L-type phase was marked with a dashed line.

From the presented diagram it follows that the melting temperature of the L-type phase increases along with the increase of cobalt content, i.e. in the range from 970 to $990 \pm 5^\circ\text{C}$.

It was also established how the composition of this phase influence the size of its unit cell. The powder diffraction patterns of samples 14, 15 and 16 were subjected to indexing. The calculated unit cell parameters of the studied phase were compiled in Table 2 depending on its composition. It follows from the presented data that the volume of the unit cell of the investigated phase increases together with the rise of the cobalt content.

Conclusions

- The composition of the howarddevansite type structure phase, crystallizing in the $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$ system, corresponds with the $\text{Co}_{2.616}\text{Fe}_{4.256}\text{V}_6\text{O}_{24}$ formula ($\text{Co}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$, where $x = -0.256$).
- The lyonsite type structure phase, crystallizing in the $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$ system has a homogeneity range with the $\text{Co}_{3+1.5x}\text{Fe}_{4-x}\text{V}_6\text{O}_{24}$ formula ($0.476 < x < 1.667$).
- The melting temperature and the unit cell volume of the lyonsite type structure phase increase together with the increase of cobalt content in this phase.

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