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REACTIVITY OF $FeVO_4$ TOWARDS $Zn_2V_2O_7$

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Abstract

The reactivity of iron(III) orthovanadate(V) towards zinc divanadate(V) in the solid state was investigated over the whole component concentration range. On the base of DTA and XRD measurements the phase diagram of the $FeVO_4$–$Zn_2V_2O_7$ system in the subsolidus area was constructed for the whole component concentration range.

Keywords: DTA, iron(III) orthovanadate(V), phase equilibria, reactivity, XRD, zinc divanadate(V)

Introduction

Hitherto published works have made it known that iron(III) orthovanadate(V) reacts in the solid state with zinc divanadate(V) forming a compound $Zn_2FeV_3O_{11}$ [1]. This compound was obtained at the same time by Wang and co-workers [2]. $Zn_2FeV_3O_{11}$ crystallizes in the triclinic system, space group P-1 [2]. Its melting temperature is equal to 851±2°C [2]. According to our recent investigations, $Zn_2FeV_3O_{11}$ melts incongruently at 835±5°C with a deposition of β-$Zn_2V_2O_7$ and $ZnFe_2O_4$ crystals [3].

The properties and the structure of $FeVO_4$ and $Zn_2V_2O_7$ are known. Iron(III) orthovanadate(V) is one of two vanadates being formed in the system Fe_2O_3–V_2O_5 [4–6]. It melts incongruently depositing solid α-Fe_2O_3 at the temperature of 870 [4] or 850°C [5]. $FeVO_4$ crystallizes in the triclinic system, space group P-1 [7]. Under normal pressure it does not display polymorphism, however its high-pressure modifications are known: one monoclinic and two orthorhombic ones [8, 9].

Zinc divanadate(V) is formed beside three other vanadates in the system ZnO–V_2O_5 [10–13]. The temperature of congruent melting of this compound, as reported by various authors, is equal to 890 [10], 877 [11] or 870°C [12]. $Zn_2V_2O_7$ occurs in two polymorphic modifications and the temperature of their reversible transformation $\alpha\text{-}Zn_2V_2O_7 \leftrightarrow \beta\text{-}Zn_2V_2O_7$ amounts according to various authors to 620 [10], 615 [11] or 590°C [12]. The α-$Zn_2V_2O_7$ polymorph crystallizes in the monoclinic system, space group C2/c [14]. The structure of the high-temperature polymorph has not been determined yet. It is only known that β-$Zn_2V_2O_7$ is isostructural with tortveitite [14].

The reactivity of iron(III) orthovanadate(V) and zinc divanadate(V) towards each other has not been a subject of any research so far, therefore it deemed interest-

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ing to investigate how $FeVO_4$ would behave against $Zn_2V_2O_7$ in the solid state in the whole component concentration range.

Experimental

The initial reagents used were Fe_2O_3 (p.a. product of POCh, Gliwice, Poland), V_2O_5 (p.a. product of Riedel de Haën, Germany) and ZnO (p.a. product of Ubichem, England). Phases used for research were also $FeVO_4$ and $Zn_2V_2O_7$ that had been obtained as a result of heating stoichiometric mixtures of suitable oxides in the following stages:

– preparation of $FeVO_4$: 560°C (24 h)+590°C (24 h)×2
– preparation of $Zn_2V_2O_7$: 560°C (24 h)+580°C (24 h)

Fifteen mixtures of $FeVO_4$ with $Zn_2V_2O_7$ were prepared for the investigations. Portions of the reacting substances were homogenized by grinding, formed into pellets and heated for several stages in the atmosphere of air. On each heating cycle the samples were cooled down to ambient temperature, ground and examined by XRD, selected samples also by DTA. After shaping them into pastilles again they were subjected to further heating. For the verifying investigation 6 samples comprising mixtures of the phases were prepared, where the phases – as we assumed – were bound to exist at equilibrium. This assumption was based on the knowledge about the phase relations in the neighbouring areas [15] and on the ground of the presented herewith results of research. After being formed into pellets, these mixtures were heated for 72 h at temperatures lower by ca. 30°C than their melting temperatures and next cooled, ground and examined also by XRD and DTA methods.

The DTA investigations were carried out by means of a Paulik–Paulik–Erdey type derivatograph (MOM, Budapest, Hungary). The measurements were performed in the atmosphere of air in the temperature range of 20–1000°C. Portions of the samples weighing as much as 500 mg were heated in quartz crucibles at a heating rate of 10 K min^{-1}. The accuracy of reading the temperatures of thermal effects on the DTA curves – as determined on the base of repetitions – amounted to ±5°C.

The composition of the samples was determined on the ground of their powder diffraction patterns obtained using the X-ray diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia). The radiation source was a cobalt tube (CoK_α) equipped with an iron filter. The identification of the phases was conducted with the aid of XRD characteristics given in PDF cards [16] and the data supplied in the works [1, 17].

Results and discussion

Table 1 presents the composition of the initial mixtures, preparative conditions and the results of XRD analysis of the samples at equilibrium, obtained after the final heating stage. The data compiled in Table 1 imply that iron(III) orthovanadate(V) and zinc divanadate(V) are not inert towards each other. $FeVO_4$ reacts with $Zn_2V_2O_7$ yielding other phases the kind of which depends on the molar ratio of the reacting substances in the initial mixtures.

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

No.	Composition of initial mixtures/mol%		Preparative conditions	Phases detected
	$FeVO_4$	$Zn_2V_2O_7$		
1	5.00	95.00	780°C (24 h) ×2	$Zn_2FeV_3O_{11}$ $Zn_2V_2O_7$
2	15.00	85.00		
3	30.00	70.00		
4	40.00	60.00		
5	50.00	50.00	780°C (24 h) ×2	$Zn_2FeV_3O_{11}$
6	60.00	40.00	610°C (24 h) ×5+ +780°C (24 h)	$Zn_2FeV_3O_{11}$ $Zn_3Fe_4(VO_4)_6$ V_2O_5
7	66.67	33.33		
8	70.00	30.00		
9	72.73	27.27	610°C (24 h) ×5+ +780°C (24 h)	$Zn_3Fe_4(VO_4)_6$ V_2O_5

In the reactants concentration up to ~50.00 mol% $FeVO_4$ this compound enters entirely into reaction with $Zn_2V_2O_7$ giving $Zn_2FeV_3O_{11}$ according to the equation:

$$FeVO_4(s)+Zn_2V_2O_7(s)=Zn_2FeV_3O_{11}(s) \tag{1}$$

The excessive reacting substance is $Zn_2V_2O_7$, so in this concentration range the occurring reaction (1) leads to obtaining a mixture of $Zn_2FeV_3O_{11}$ and $Zn_2V_2O_7$. At a molar ratio of $FeVO_4/Zn_2V_2O_7$ equal to 1:1 both compounds react with each other completely giving $Zn_2FeV_3O_{11}$. This is evidenced by the composition of the sample obtained as a result of heating a mixture of 50.00 mol% $FeVO_4$ and 50.00 mol% $Zn_2V_2O_7$.

Samples containing in the initial mixtures more than 50.00 mol% up to 72.73 mol% $FeVO_4$ were heated at 610°C in several stages. Results of XRD investigations of the samples obtained after the respective stages showed that zinc divanadate(V) had reacted until completion and the samples contained $Zn_2FeV_3O_{11}$, $FeVO_4$ and $Zn_3Fe_4(VO_4)_6$. On further heating stages at 610°C the composition of the samples did not change, but only with increasing the heating time an increase of $Zn_3Fe_4(VO_4)_6$ content and a decrease of $FeVO_4$ and $Zn_2FeV_3O_{11}$ contents were observed. This should be indicative of the fact that $Zn_2FeV_3O_{11}$ formed during the reaction (1) reacts with iron(III) orthovanadate(V), as a result of which $Zn_3Fe_4(VO_4)_6$ is formed. There must be then another phase among the phases formed in the reaction mixtures although its presence could not be detected by the XRD method. Considering a total using up of $FeVO_4$ in the reaction with $Zn_2FeV_3O_{11}$ or $Zn_2V_2O_7$ this phase should be V_2O_5, which can be expressed by the equations that follow:

$$3Zn_2FeV_3O_{11}(s)+5FeVO_4(s)= 2Zn_3Fe_4(VO_4)_6(s)+V_2O_5(s) \tag{2}$$

or

$$8FeVO_4(s)+3Zn_2V_2O_7(s)=2Zn_3Fe_4(VO_4)_6(s)+V_2O_5(s) \tag{3}$$

During the syntheses conducted at 610°C $FeVO_4$ could not be used up completely.

All samples from this component concentration range were additionally heated at 780°C and next very slowly cooled.

The presence of $FeVO_4$ was no longer detected in the samples containing from ~50.00 to ~72.73 mol% of iron(III) orthovanadate(V). Now these samples comprised a mixture of three phases: $Zn_2FeV_3O_{11}$, $Zn_3Fe_4(VO_4)_6$ and V_2O_5. Thus the reaction occurring between the previously formed $Zn_2FeV_3O_{11}$ and $FeVO_4$ yielded $Zn_3Fe_4(VO_4)_6$ and V_2O_5. The composition of the sample obtained after heating a mixture containing 72.73 mol% $FeVO_4$ and 27.27 mol% $Zn_2V_2O_7$ in the initial mixtures proves that this reaction takes place quantitatively according to Eq. (2) or (3).

In the remaining component concentration range, i.e. above 72.73 mol% $FeVO_4$ in the initial mixtures, by performing the synthesis at 610°C, the obtaining of samples at equilibrium also could not be achieved. A greater excess of $FeVO_4$ in relation to $Zn_2V_2O_7$ should cause an appearance of $Fe_2V_4O_{13}$ beside $Zn_3Fe_4(VO_4)_6$ in the system, which can be described by the equation:

$$10FeVO_4(s)+3Zn_2V_2O_7(s)=2Zn_3Fe_4(VO_4)_6(s)+Fe_2V_4O_{13}(s) \quad (4)$$

This supposition is supported by the results of our other investigations [15] on the phase relations in the system $ZnO–V_2O_5–Fe_2O_3$. The $Fe_2V_4O_{13}$ phase was not successfully obtained in any prepared sample. Attempts of obtaining preparations at equilibrium after their melting and very gradual cooling also did not result in a positive outcome because of the incongruent melting of $Fe_2V_4O_{13}$ at 665°C [5]. The product identified in the samples was always $FeVO_4$ resulting from the melting and also V_2O_5.

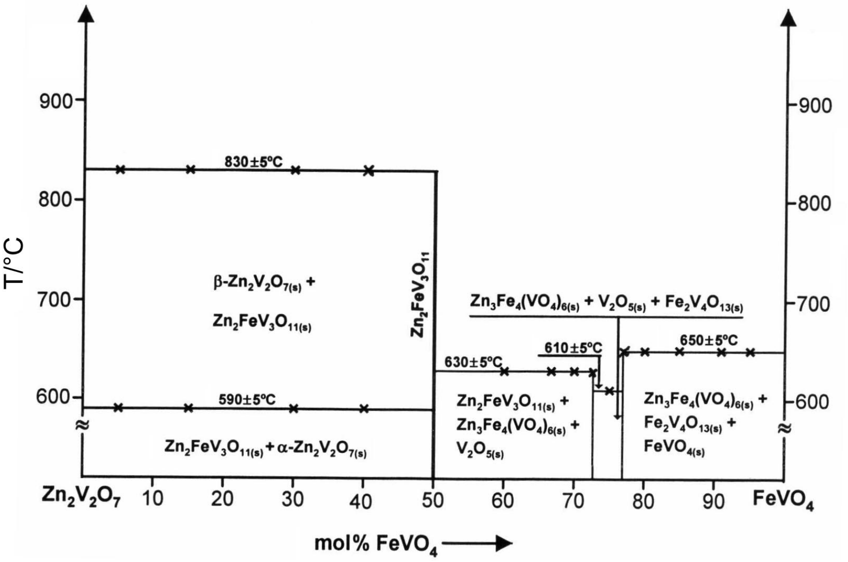

Fig. 1 Phase diagram in the subsolidus area of the $FeVO_4–Zn_2V_2O_7$ system

A further stage of this work was constructing a phase diagram of the subsolidus area of the system $FeVO_4$–$Zn_2V_2O_7$. The conducted research proved to be insufficient for describing the phase equilibria being established in the system under consideration in the components concentration range above 72.73 mol% $FeVO_4$ with respect to initial mixtures. It appeared therefore necessary to perform verifying investigations in order to check what phases co-exist at equilibrium in this component concentration range. Six mixtures of phases found to be at equilibrium with one another according to the hitherto carried out research were prepared. The composition of these mixtures is listed in Table 2. The phase composition of the prepared samples, despite their many-hour heating at temperatures close to their melting point, did not change at all. This proves that the initial mixtures corresponded as to their composition to the previously determined phases co-existing at equilibrium.

Table 2 The composition of the verifying mixtures and the composition of the verifying mixtures in terms of the components of the system

No.	Composition of verifying mixtures	Composition of verifying mixtures in terms of components of the system/mol%	
		$FeVO_4$	$Zn_2V_2O_7$
1	$Zn_3Fe_4(VO_4)_6$, V_2O_5, $Fe_2V_4O_{13}$	75.00	25.00
2	$Zn_3Fe_4(VO_4)_6$, $Fe_2V_4O_{13}$	76.92	23.08
3	$Zn_3Fe_4(VO_4)_6$, $Fe_2V_4O_{13}$, $FeVO_4$	80.00	20.00
4		85.00	15.00
5		90.00	10.00
6		95.00	5.00

The phase diagram of the system $FeVO_4$–$Zn_2V_2O_7$ (Fig. 1) in the subsolidus area was constructed on the base of DTA curves and results of XRD examination of the samples at equilibrium (up to 72.73 mol% $FeVO_4$ in the initial mixtures) as well as of additional samples verifying the remaining component concentration range (above 72.73 mol% $FeVO_4$ in the initial mixtures). The temperature of the solidus line was determined on the ground of the onset temperatures of the first endothermic effects, being not the effects of polymorphic transformations, recorded on the DTA curves of both the samples at equilibrium and the verifying samples. The line of the polymorphic transformation α-$Zn_2V_2O_7 \leftrightarrow \beta$-$Zn_2V_2O_7$ is also marked on the diagram.

The presented diagram shows that the $FeVO_4$–$Zn_2V_2O_7$ system is a real binary system in the subsolidus area in the concentration range up to 50.00 mol% $FeVO_4$. In the remaining concentration range the investigated system is an intersection of the ternary system ZnO-V_2O_5–Fe_2O_3 and crosses the following subsidiary subsystems:

$$Zn_2FeV_3O_{11}–Zn_3Fe_4(VO_4)_6–V_2O_5$$

$$Zn_3Fe_4(VO_4)_6–V_2O_5–Fe_2V_4O_{13}$$

$$Zn_3Fe_4(VO_4)_6–Fe_2V_4O_{13}–FeVO_4$$

Conclusions

Iron(III) orthovanadate(V) reacts with zinc divanadate(V) and depending on the molar ratio of the reacting substances in the initial mixtures various compounds are formed.

The $FeVO_4$–$Zn_2V_2O_7$ system is a real binary system only in the concentration range up to 50.00 mol% $FeVO_4$ in the initial mixtures. In the remaining concentration range it is an intersection of the ternary system ZnO–V_2O_5–Fe_2O_3.

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