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# PHASE RELATIONS IN THE SYSTEM $ZnV_2O_6$–$ZnFe_2O_4$

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## Abstract

Using DTA and XRD methods, a diagram of phase equilibria in $ZnV_2O_6$–$ZnFe_2O_4$ system has been constructed. System $ZnV_2O_6$–$ZnFe_2O_4$ is in subsolidus area a real binary system and its components form a compound $Zn_2FeV_3O_{11}$. $Zn_2FeV_3O_{11}$ melts incongruently at 835±5ºC with deposition of two solid phases: β-$Zn_2V_2O_7$ and $ZnFe_2O_4$.

**Keywords:** DTA, phase diagram, $ZnFe_2O_4$, $ZnV_2O_6$, XRD

## Introduction

Properties and structure of the components of the $ZnV_2O_6$–$ZnFe_2O_4$ system are well known. Zinc metavanadate(V) is one of four compounds being formed in the system $V_2O_5$–ZnO [1]. $ZnV_2O_6$ crystallises in the monoclinic system, space group C2/m [2] and it exhibits a brannerite-type structure [3]. $ZnV_2O_6$ melts incongruently according to [4] and to our investigations, at 650±5°C [1, 4]. Other authors have determined this melting temperature as equal to 654 [3] or 660°C [5]. Solid product of melting $ZnV_2O_6$ is β-$Zn_2V_2O_7$ [1–5]. The other component of the investigated system – $ZnFe_2O_4$ – is the only compound being formed in the system ZnO–$Fe_2O_3$ under normal conditions [6,7]. $ZnFe_2O_4$ possesses a structure of spinel [8–10] and crystallises in the regular system, space group Fd3m [6,7,11]. The melting temperature of $ZnFe_2O_4$ has been determined as equal to 1590°C [12].

According to our investigations, $ZnV_2O_6$ and $ZnFe_2O_4$ mixed at a molar ratio of 3:1 react with each other in the solid state forming a compound of a formula $Zn_2FeV_3O_{11}$ [13]. This compound was obtained at the same time by Wang and co-workers [14]. $Zn_2FeV_3O_{11}$ crystallises in the triclinic system, space group P-1; it is isostructural with $GaMg_xZn_{2-x}V_3O_{11}$ [14]. The melting temperature of $Zn_2FeV_3O_{11}$ amounts to 851±2°C [14].

The presented work aimed to work out a diagram of phase equilibria being established in the $ZnV_2O_6$–$ZnFe_2O_4$ system over the whole component concentration range up to 1000°C.

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## Experimental

The reagents used for research were: ZnO p.a. (Ubichem, England), $V_2O_5$ p.a. (Riedel-de Haën, Germany) and $\alpha$-$Fe_2O_3$ p.a. (VEB Laborchemie Apolda, Germany) sintered at 1000°C in three 48 h stages. For the investigations 12 samples were prepared comprising the whole component concentration range of the system under consideration. The oxides were weighed in appropriate portions, thoroughly homogenised by grinding, shaped into pellets and heated in several stages in the atmosphere of air. After each heating stage the samples were cooled down at room temperature with an average cooling rate of 10ºC $min^{-1}$, ground and subjected to examination by XRD and DTA methods. Then they were shaped into pellets again and heated, and the whole procedure was repeated until preparations at equilibrium were obtained. In order to determine the kind of phases remaining at equilibrium with liquid, selected samples having attained equilibrium were additionally heated for 4–6 h at chosen temperatures. On completion of heating, the samples were rapidly cooled down at room temperature ('frozen'), ground and analysed by means of XRD method.

The DTA/TG measurements with the use of a Paulik–Paulik–Erdey derivatograph (MOM, Hungary) were performed under air in quartz crucibles at a heating rate of 10ºC $min^{-1}$ over the range of 20–1000°C. The mass of the investigated samples amounted always to 500 mg. Selected samples were examined by using the SDT 2960 apparatus (TA Instruments, USA) at a heating rate of 5ºC $min^{-1}$ under nitrogen atmosphere. The reference substance was $\alpha$-$Al_2O_3$. The melting temperature was read as the onset temperature of the endothermic effect recorded on the DTA curve.

The XRD investigations were carried out using a diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, Russia) and applying the radiation $CoK_\alpha$/Fe. Identification of individual phases was conducted on the data base contained in the JC PDF cards [15] and in [13].

## Results and discussion

The research was begun with a verification of the way and the melting temperature of $Zn_2FeV_3O_{11}$. The melting temperature of $Zn_2FeV_3O_{11}$, read from the DTA curve (Fig. 1b) as the onset of the endothermic effect observed, amounts to 835±5°C. Results of XRD analysis of the compound $Zn_2FeV_3O_{11}$ melted at 845°C and then rapidly cooled down at room temperature have shown that $Zn_2FeV_3O_{11}$ melts incongruently with a deposition of two solid phases, i. e. $\beta$-$Zn_2V_2O_7$ and $ZnFe_2O_4$:

$$Zn_2FeV_3O_{11(s)} \xleftrightarrow{835\pm5^\circ C} \beta\text{-}Zn_2V_2O_{7(s)} + ZnFe_2O_{4(s)} + \text{liquid} \quad (1)$$

The other endothermic effect recorded on the DTA curve for the compound $Zn_2FeV_3O_{11}$ (Fig. 1b) is associated with crossing the liquidus temperature.

Table 1 lists the composition of initial mixtures, preparation conditions and the results of XRD analysis for all samples having attained equilibrium. Data compiled in this table imply that the system $ZnV_2O_6$–$ZnFe_2O_4$ components are not inert towards each other and react in the solid state according to the equation:

$$3ZnV_2O_{6(s)} + ZnFe_2O_{4(s)} = 2Zn_2FeV_3O_{11(s)} \quad (2)$$

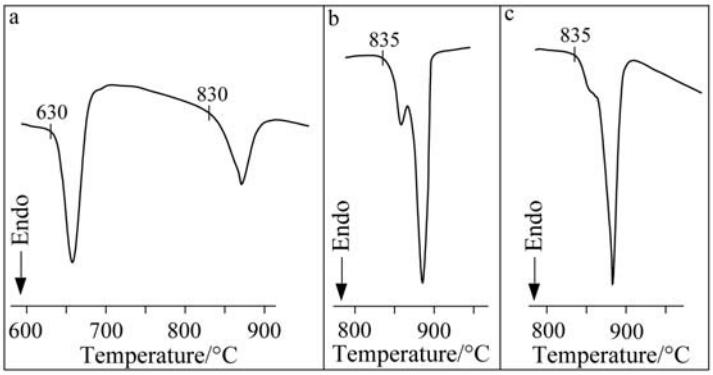


**Fig. 1** DTA curves of selected samples at equilibrium: a – comprising 90 mol% $ZnV_2O_6$ in initial mixture; b – $Zn_2FeV_3O_{11}$; c – comprising 60 mol% $ZnV_2O_6$ in initial mixture

**Table 1** Composition of initial mixtures, preparation conditions and results of XRD analysis for samples at equilibrium

| No. | Composition of initial mixtures in terms of the components for investigated system/mol% | | Preparation conditions | Composition of samples at equilibrium |
|---|---|---|---|---|
| | $ZnV_2O_6$ | $ZnFe_2O_4$ | | |
| 1 | 10.00 | 90.00 | 550°C(24 h)+ 580°C (24 h)+ 650°C (24 h)+ 750°C (24 h)+ 800°C (24 h×2) | $Zn_2FeV_3O_{11}$, $ZnFe_2O_4$ |
| 2 | 20.00 | 80.00 | | |
| 3 | 40.00 | 60.00 | | |
| 4 | 50.00 | 50.00 | | |
| 5 | 60.00 | 40.00 | | |
| 6 | 75.00 | 25.00 | | $Zn_2FeV_3O_{11}$ |
| 7 | 80.00 | 20.00 | 550°C (24 h)+ 580°C (40 h)+ 600°C (10 h+24 h) | $Zn_2FeV_3O_{11}$, $ZnV_2O_6$ |
| 8 | 82.50 | 17.50 | | |
| 9 | 85.00 | 15.00 | | |
| 10 | 87.50 | 12.50 | | |
| 11 | 90.00 | 10.00 | | |
| 12 | 93.00 | 7.00 | | |

As a consequence the compound $Zn_2FeV_3O_{11}$ is formed. A corroboration of the quantitative completion of reaction (1) is the composition of a sample corresponding to 75.00 mol% $ZnV_2O_6$ and 25 mol% $ZnFe_2O_4$ in the initial mixture. In the component concentration range up to 75.00 mol% $ZnV_2O_6$, zinc metavanadate(V) reacts till completion with $ZnFe_2O_4$. In this component concentration range the solid phase co-existing at equilibrium with the product of reaction (1) is $ZnFe_2O_4$. In the remaining component concentration range, i.e. above 75.00 mol% $ZnV_2O_6$ in the initial mix-

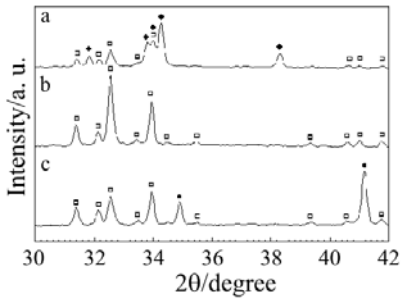


**Fig. 2** Comparative drawing of XRD patterns of selected samples at equilibrium: a – comprising 90 mol% $ZnV_2O_6$ in initial mixture; b – $Zn_2FeV_3O_{11}$; c – comprising 60 mol% $ZnV_2O_6$ in initial mixture. ◆ – lines characteristic of $ZnV_2O_6$; □ – lines characteristic of $Zn_2FeV_3O_{11}$; ● – lines characteristic of $ZnFe_2O_4$

tures, the reacting substance occurring in excess, according to Eq. (1) is $ZnV_2O_6$. In this component concentration range, $Zn_2FeV_3O_{11}$ and $ZnV_2O_6$ co-exist in the subsolidus area. Figure 1 presents the DTA curves of samples at equilibrium selected from the subsolidus areas of the investigated system and the curve of $Zn_2FeV_3O_{11}$, whereas Fig. 2 – the diffraction patterns of these samples.

Figure 3 presents a phase diagram of the system $ZnV_2O_6$–$ZnFe_2O_4$ as worked out on the base of the DTA curves and the results of XRD analysis for the samples at equilibrium and the 'frozen' samples. While constructing the phase diagram, the solidus temperature line was assumed to be equal to the onset temperatures of melting effects, recorded on the DTA curves as the first. The temperature of liquidus curves was determined on the ground of the onset temperatures as well, but in this case they corresponded to the effects recorded on the DTA curves as the last.

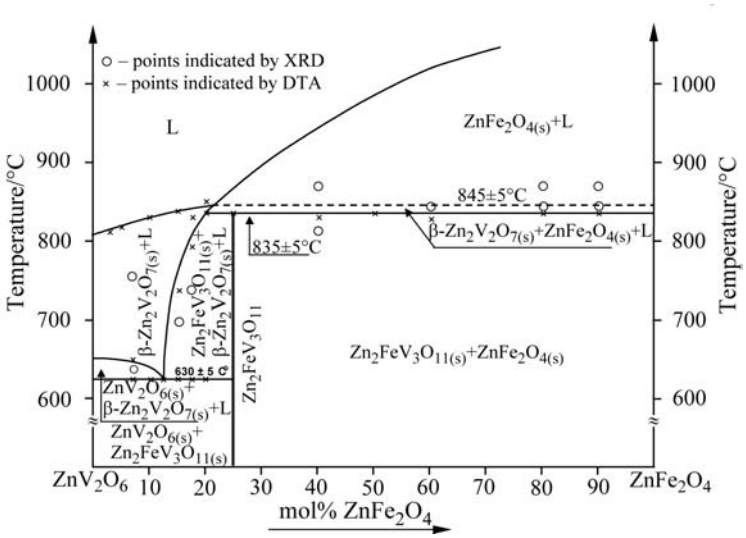


**Fig. 3** Diagram of phase equilibria of $ZnV_2O_6$–$ZnFe_2O_4$ system

It can be inferred from the presented diagram that the $ZnV_2O_6$–$ZnFe_2O_4$ system is a real binary system in the subsolidus area over the whole component concentration range and its components form the compound $Zn_2FeV_3O_{11}$. Both $Zn_2FeV_3O_{11}$ and $ZnV_2O_6$ form an eutectic mixture (about 67.0 mol% $ZnV_2O_6$ and 33.0 mol% $Zn_2FeV_3O_{11}$) melting at 630±5°C. Above the temperature of solidus line the system $ZnV_2O_6$–$ZnFe_2O_4$, regarding an incongruent way of melting both $ZnV_2O_6$ and $Zn_2FeV_3O_{11}$ ceases to be a binary system in the whole component concentration range. The temperature region of co-existence of two solid phases, β-$Zn_2V_2O_7$ and $ZnFe_2O_4$, with liquid is narrow and covers about 10° (the upper limit was determined only on the base of XRD results of 'frozen' samples). Above 845°C the phase co-existing with liquid is $ZnFe_2O_4$ only. The liquidus line of the area, where solid $ZnFe_2O_4$ remains at equilibrium with liquid, was also drawn on the base of XRD results of 'frozen' samples only.

## Conclusions

- $Zn_2FeV_3O_{11}$ melts incongruently with deposition of two solid phases: β-$Zn_2V_2O_7$ and $ZnFe_2O_4$ at 835±5ºC.
- System $ZnV_2O_6$–$ZnFe_2O_4$ is in subsolidus area a real binary system and its components form the compound $Zn_2FeV_3O_{11}$.
- Both $Zn_2FeV_3O_{11}$ and $ZnV_2O_6$ form an eutectic mixture (about 67.0 mol% $ZnV_2O_6$ and 33.0 mol% $Zn_2FeV_3O_{11}$) melting at 630±5°C.

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