

## STUDIES ON THE SYSTEM $\text{ZnO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ Reactivity of $\text{ZnFe}_2\text{O}_4$ towards $\text{ZnV}_2\text{O}_6$

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### Abstract

Studies on the reactivity of  $\text{ZnFe}_2\text{O}_4$  towards  $\text{ZnV}_2\text{O}_6$  revealed that in the solid state the phases interact in a molar ratio of 1:3 to form a new compound, to which the molecular formula  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$  was assigned. The compound melts congruently at  $825\pm 5^\circ\text{C}$ .

**Keywords:** DTA, iron(III), reactivity, XRD, zinc ferrite, zinc metavanadate, zinc oxide

### Introduction

Our recent studies on the three-component oxide systems  $\text{NiO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$  and  $\text{CuO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$  demonstrated that the components of these systems interact in the solid state. The reactions involving all three oxides lead to new compounds distinguished by interesting structural and magnetic properties [1-4]. Thus, it seemed worthwhile to undertake works on analogous systems of interest. The first system selected for study of the novel phases formed by reaction between the components was the three-component system  $\text{ZnO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ .

The system  $\text{ZnO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$  is built up from the three two-component systems:  $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3\text{-ZnO}$  and  $\text{V}_2\text{O}_5\text{-ZnO}$ . These systems are well known, having been investigated comprehensively earlier. The components of the system  $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$  interact to produce two compounds,  $\text{Fe}_2\text{V}_4\text{O}_{13}$  and  $\text{FeVO}_4$ , with recognisable structure and thermal properties [5, 6]. The system  $\text{Fe}_2\text{O}_3\text{-ZnO}$  includes only one compound,  $\text{ZnFe}_2\text{O}_4$  [7], while the system  $\text{V}_2\text{O}_5\text{-ZnO}$  forms three compounds,  $\text{ZnV}_2\text{O}_6$ ,  $\text{Zn}_2\text{V}_2\text{O}_7$  and  $\text{Zn}_3\text{V}_2\text{O}_8$ , and one metastable phase  $\text{Zn}_4\text{V}_2\text{O}_9$  [8, 9].

It was considered worthwhile to observe the reactivity of  $\text{ZnFe}_2\text{O}_4$  towards  $\text{ZnV}_2\text{O}_6$  in the solid state.

The structures and some properties of both reagents have been recognized. Zinc metavanadate can be obtained by the reaction in the solid state at  $550^\circ\text{C}$  of an equimolar  $\text{ZnO/V}_2\text{O}_5$  mixture [8]. The compound crystallizes in the monoclinic system, space group  $\text{C2/m}$  or  $\text{C2}$  [10], and melts incongruently at  $645^\circ\text{C}$  to deposit  $\beta\text{-Zn}_2\text{V}_2\text{O}_7$ , a phase stable at this temperature [11, 12].  $\text{ZnFe}_2\text{O}_4$  is a ferrite with a spinel-type

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structure. The compound can be obtained by a reaction between ZnO and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, taking place in the solid state at 800°C [7] or by co-precipitation of an equimolar mixture of hydroxides followed by calcination at 600 and 800°C [13]. ZnFe<sub>2</sub>O<sub>4</sub> crystallizes in a regular system, space group Fd3m [14], and melts incongruently at 1590°C.

## Experimental

The following reagents were used in the experiments:

- ZnO – analytical reagent (Ubichem, England),
- V<sub>2</sub>O<sub>5</sub> – analytical reagent (POCh, Glivice, Poland),
- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> – analytical reagent (VEB, Germany), heated at 1000°C in three 24-h stages,
- ZnFe<sub>2</sub>O<sub>4</sub> – prepared by the method reported in [7],
- ZnV<sub>2</sub>O<sub>6</sub> – prepared by the method reported in [8],
- FeVO<sub>4</sub> – prepared by the method reported in [5],
- Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> – prepared by the method reported in [15].

The reagents were weighed in suitable proportions, homogenized by grinding, and shaped into pastilles, which were then heated in the solid state. After each heating stage, the samples were carefully cooled to ambient temperature, ground and analysed by DTA and XRD methods. Afterwards, the samples were again shaped into pastilles and heated further. The temperatures of the consecutive heating stages were fixed on the basis of the DTA results.

The DTA measurements were made by using a derivatograph of Paulik-Paulik-Erdey type (MOM, Budapest, Hungary) at 20–1000°C. Samples with a mass of 1000 mg were placed in quartz crucibles and heated at a rate of 10°C min<sup>-1</sup>. Repeated DTA measurements on a given sample revealed that the accuracy of temperature reading was  $\pm 5^\circ\text{C}$ .

X-ray phase diffractometry was based upon diffraction patterns recorded with a DRON-3 instrument (Dobrovestnik, St. Petersburg, Russia). A cobalt lamp with an Fe filter was used as radiation source. Phases were identified via the X-ray characteristics included in PDF cards [16].

## Results and discussion

Two series of samples were prepared for the experiments. The reagents in the first series were the oxides of the system ZnO–V<sub>2</sub>O<sub>5</sub>–Fe<sub>2</sub>O<sub>3</sub>, while those in the other series were reactants ZnFe<sub>2</sub>O<sub>4</sub> and ZnV<sub>2</sub>O<sub>6</sub>. The samples in the first series were heated in the following way: 450°C→500°C (24 h)+550°C (24 h)+580°C (24 h×2)+600°C (24 h×2), and the samples in the other series were heated as follows: 550°C (24 h)+580°C (24 h)+600°C (24 h×3).

Table 1 details the contents of the initial mixtures in both series and the results of X-ray phase analysis on samples after the final heating stage. Irrespective of the types of reagents used for the reactions and the contents of the initial mixtures, the

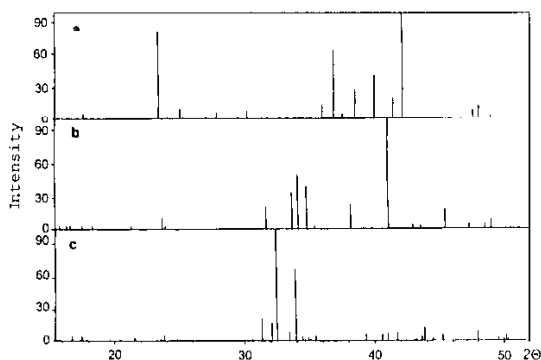
**Table 1** Contents of initial mixtures in both examined series, and results of X-ray diffraction analysis of samples after the final heating stage

| No. | Contents of initial mixtures in series 1/mol% |                               |                                | Contents of initial mixtures in series 2/mol% |                                 | Phases detected                      |
|-----|---|-------------------------------|--------------------------------|---|---------------------------------|--------------------------------------|
|     | ZnO   | V <sub>2</sub> O <sub>5</sub> | Fe <sub>2</sub> O <sub>3</sub> | ZnFe <sub>2</sub> O <sub>4</sub>              | ZnV <sub>2</sub> O <sub>6</sub> |                                      |
| 1   | 50.00   | 12.50                         | 37.50                          | 75.00   | 25.00                           | N*, ZnFe <sub>2</sub> O <sub>4</sub> |
| 2   | 50.00   | 16.67                         | 33.33                          | 66.67   | 33.33                           | N*, ZnFe <sub>2</sub> O <sub>4</sub> |
| 3   | 50.00   | 25.00                         | 25.00                          | 50.00   | 50.00                           | N*, ZnFe <sub>2</sub> O <sub>4</sub> |
| 4   | 50.00   | 31.25                         | 18.75                          | 37.50   | 62.50                           | N*, ZnFe <sub>2</sub> O <sub>4</sub> |
| 5   | 50.00   | 33.33                         | 16.67                          | 66.67   | 33.33                           | N*, ZnFe <sub>2</sub> O <sub>4</sub> |
| 6   | 50.00   | 37.50                         | 12.50                          | 25.00   | 75.00                           | N*                                   |
| 7   | 50.00   | 38.89                         | 11.11                          | 22.22   | 77.78                           | N*, ZnV <sub>2</sub> O <sub>6</sub>  |
| 8   | 50.00   | 41.67                         | 8.33                           | 16.67   | 83.33                           | N*, ZnV <sub>2</sub> O <sub>6</sub>  |

N\* – the phase characterized by a new set of diffraction lines

diffraction patterns demonstrated a set of lines which could not be attributed to any of the known phases of the three-component system.

The diffraction patterns of samples initially containing 50.00 mol% of ZnO+37.50, 33.33, 25.00, 18.75 or 16.67 mol% of Fe<sub>2</sub>O<sub>3</sub>+12.50, 16.67, 25.00, 31.25 or 33.33 mol% of V<sub>2</sub>O<sub>5</sub> exhibited a novel set of diffraction lines and a line set characteristic of the phase ZnFe<sub>2</sub>O<sub>4</sub>. On the other hand, the diffraction patterns of samples initially containing 12.50 mol% of Fe<sub>2</sub>O<sub>3</sub>+37.50 mol% V<sub>2</sub>O<sub>5</sub>+50.00 mol% of ZnO (25.00 mol% of ZnFe<sub>2</sub>O<sub>4</sub>+75 mol% of ZnV<sub>2</sub>O<sub>6</sub>) displayed only the new set of diffraction lines. The diffraction patterns of samples initially containing 50.00 mol% of ZnO+11.11 or 8.33 mol% of Fe<sub>2</sub>O<sub>3</sub>+38.89 or 41.47 mol% of V<sub>2</sub>O<sub>5</sub> included a novel set of lines and a line set characteristic of ZnV<sub>2</sub>O<sub>6</sub>.



**Fig. 1** Diffraction patterns: a – mixture with initial content 50.00 mol% of ZnO+37.50 mol% of V<sub>2</sub>O<sub>5</sub>+12.50 mol% of Fe<sub>2</sub>O<sub>3</sub>; b – mixture with initial content 25.00 mol% of ZnFe<sub>2</sub>O<sub>4</sub>+75.00 mol% of ZnV<sub>2</sub>O<sub>6</sub>; c – the new phase Zn<sub>2</sub>FeV<sub>3</sub>O<sub>11</sub>

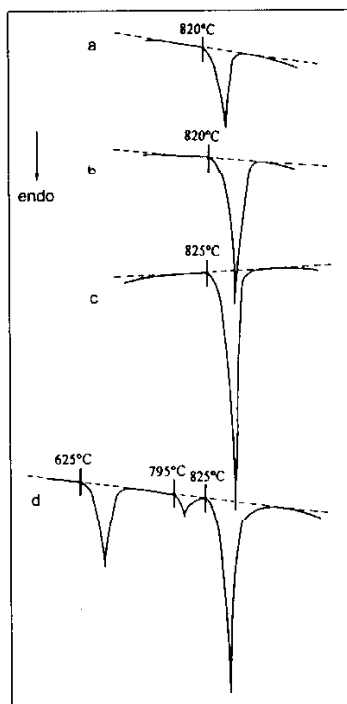


Fig. 2 DTA curves of selected samples in the first series after the final heating stage,  $ZnV_2O_6$  and  $ZnFe_2O_4$  in a molar ratio of a – 0.33:1; b – 1.67:1; c – 3:1; d – 5:1

Table 2 Results of X-ray diffraction analysis of the sample initially containing 50.00 mol% of  $Zn_3V_5O_{17}$  + 50.00 mol% of  $FeVO_4$ , after consecutive heating stages

| No. | Temperature/ $^{\circ}C$ | Heating time/h | Phases detected                              |
|-----|--------------------------|----------------|--|
| 1   | 600                      | 18             | $FeVO_4$ , $Zn_2V_2O_7$ , N*                 |
| 2   | 600                      | 24             | N*, $FeVO_4$ – traces, $Zn_2V_2O_7$ – traces |
| 3   | 700                      | 24             | N*   |

N\* – the phase characterized by a new set of diffraction lines

Figure 1 presents diffraction patterns of initial mixtures composed of 12.50 mol% of  $Fe_2O_3$ +37.50 mol% of  $V_2O_5$ +50.00 mol% of  $ZnO$ , or 25.00 mol% of  $ZnFe_2O_4$ +75 mol% of  $ZnV_2O_6$ , against diffraction patterns of the samples obtained after the final heating stage. In order to support the findings, a single synthesis of the novel phase was performed, using the reactants  $ZnV_2O_7$  and  $FeVO_4$  in 1:1 molar ratio. Table 2 reports the XRD analysis data on samples for each heating stage. The set of diffraction lines characteristic of the phase prepared from the above reactants ap-

peared to be fully consistent with the diffraction pattern of the sample obtained from 25.00 mol% of  $\text{ZnFe}_2\text{O}_4$ +75 mol% of  $\text{ZnV}_2\text{O}_6$ . Accordingly, the molecular formula  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$  was attributed to the new phase.

The DTA curves of the investigated samples in both series displayed one or three endothermic effects after the final heating cycle (Fig. 2). The endothermic effect recorded in the DTA curves of samples 1–6, with the beginning of the endothermic peak at  $820\pm 5^\circ\text{C}$ , may be regarded as reflecting melting of the new phase  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$ . The DTA curves of the remaining samples exhibited three effects with the temperatures of the beginning of the endothermic peaks at  $640\pm 5$ ,  $790\pm 5$  and  $820\pm 5^\circ\text{C}$ . The first of these peaks seems to correspond to incongruent melting of  $\text{ZnV}_2\text{O}_6$  and afterwards  $\text{Zn}_2\text{V}_2\text{O}_7$ , the second peak to a polymorphic transformation of  $\text{Zn}_3\text{V}_2\text{O}_8$  [12], and the third to melting of the phase mixture with  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$  as one component.

A sample of the new phase was heated at  $860^\circ\text{C}$  for 5 h and then quenched to ambient temperature. The appearance of the sample taken out of the furnace suggested that the sample had melted. X-ray phase diffraction of the sample prepared in this way demonstrated that  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$  melts congruently.

## Summary

The experimental results can be summarized as follows:

1. The phases  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnV}_2\text{O}_6$  occurring in the three-component system  $\text{ZnO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$  in the solid state are not inert to each other and interact to produce a new compound, to which the molecular formula  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$  was attributed.

2. The compound  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$  can be prepared in a reaction in the solid state between the reagents and/or reactants of any of the sets specified below:

- $\text{ZnO}$ ,  $\text{V}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$  in a molar ratio of 1:3:4
- $\text{ZnV}_2\text{O}_6$  and  $\text{ZnFe}_2\text{O}_4$  in a molar ratio of 3:1, or
- $\text{Zn}_2\text{V}_2\text{O}_7$  and  $\text{FeVO}_4$  in a molar ratio of 1:1.

3. The compound  $\text{Zn}_2\text{FeV}_3\text{O}_{11}$  melts congruently at  $825\pm 5^\circ\text{C}$ .

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