

SYNTHESIS AND PROPERTIES OF THE SOLID SOLUTIONS FORMED IN THE $\text{Fe}_2\text{V}_4\text{O}_{13}$ – $\text{Cr}_2\text{V}_4\text{O}_{13}$ SYSTEM

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Abstract

DTA and XRD studies of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ – $\text{Cr}_2\text{V}_4\text{O}_{13}$ system have shown that continuous solid solutions of a $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ type, bearing a $\text{Fe}_2\text{V}_4\text{O}_{13}$ structure, are formed in the system. With the increasing degree of the Cr^{3+} ion incorporation into the $\text{Fe}_2\text{V}_4\text{O}_{13}$ structure, a contraction of the solid solution crystal lattice develops. Solid solutions of a $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ type melt incongruently, their melting temperature increasing from 953 to 1003 K with increase in the degree of the Cr^{3+} ion incorporation. The solid product of melting $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ solid solutions for $0.2 < x < 1.2$ is the $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ solution phase, and for $x \leq 0.2$ and $x \geq 1.4$ – the $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ phase as well as FeVO_4 or CrVO_4 , respectively.

Keywords: DTA, $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ solid solutions, XRD

Introduction

A literature scan has provided information that components of the systems V_2O_5 – Cr_2O_3 and V_2O_5 – Fe_2O_3 , react in the solid state to form compounds of an MVO_4 or $\text{M}_2\text{V}_4\text{O}_{13}$ type, where $M = \text{Cr}$ or Fe [1, 2]. The $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ phase is known to crystallise in the two-component FeVO_4 – CrVO_4 system [3–6]. Some workers maintain that the phase is a chemical compound with a formula $\text{FeCr}(\text{VO}_4)_2$ ($\text{Fe}_{0.5}\text{Cr}_{0.5}\text{VO}_4$) [3, 4]. Still others think that it is a phase of a solid solution type being formed between FeVO_4 and CrVO_4 , with a very great homogeneity range, that is, for $0.2 < x < 0.8$ [5, 6]. The experimental results have shown that the $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ solid solutions crystallise in a monoclinic system and are isostructural with α - MnMoO_4 [5]. Thus, the structure of the $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ phase differs essentially from the structures of FeVO_4 (triclinic) and CrVO_4 (orthorhombic).

A full crystal structure of $\text{Fe}_2\text{V}_4\text{O}_{13}$ – another phase originating beside FeVO_4 in the V_2O_5 – Fe_2O_3 system – is also known [7]. $\text{Fe}_2\text{V}_4\text{O}_{13}$ crystallises in a monoclinic system, space group $\text{P}2_1/\text{c}$, $Z = 4$.

According to the information published, $\text{Fe}_2\text{V}_4\text{O}_{13}$ is isostructural with $\text{Cr}_2\text{V}_4\text{O}_{13}$, and both the compounds have very similar unit cell parameters [1].

It was deemed very interesting to find out whether the compounds, $\text{Fe}_2\text{V}_4\text{O}_{13}$ and $\text{Cr}_2\text{V}_4\text{O}_{13}$, could form solid solutions with each other and what the concentration range of their mutual solubility would be against the data published. Accordingly, some studies were carried out on the reactivity of $\text{Fe}_2\text{V}_4\text{O}_{13}$ towards $\text{Cr}_2\text{V}_4\text{O}_{13}$ over the whole component concentration range of the system built in the solid state by the compounds.

Experimental

The following reagents were used in experiments:

- $\alpha\text{-Fe}_2\text{O}_3$, an analar product of POCh (Gliwice, Poland),
- Cr_2O_3 , a pure product of Aldrich Chemie (Germany),
- V_2O_5 , an analar product of POCh (Gliwice, Poland),
- $\text{Fe}_2\text{V}_4\text{O}_{13}$ and $\text{Cr}_2\text{V}_4\text{O}_{13}$ – compounds specially prepared from oxides by the methods described in works [1, 2].

Differential thermal analysis (DTA) was carried out using a Derivatograph (MOM, Hungary). Samples of 500 mg mass were heated in air to 1273 K, at a heating rate of 10 deg min^{-1} , in quartz crucibles.

The phase composition of the samples treated thermally was determined depending on their powder diffraction patterns, taken by a diffractometer of a DRON-3 type (Bourestvnik, Sankt-Petersburg, Russia), using $\text{CoK}_\alpha/\text{Fe}$ radiation. Identification of individual phases was made with the aid of JCPDS cards and the published information [1, 5].

With the purpose of studying the mutual reactivity of components of the $\text{Fe}_2\text{V}_4\text{O}_{13}\text{-Cr}_2\text{V}_4\text{O}_{13}$ system, 9 samples were prepared from the oxides: Fe_2O_3 , Cr_2O_3 and V_2O_5 , so matched as to cover the whole component concentration range of the system under study. Table 1 shows compositions of the samples prepared. Within the scope of this research, two mixtures comprising 30.00 and 70.00 mol% of $\text{Cr}_2\text{V}_4\text{O}_{13}$ were also prepared from $\text{Fe}_2\text{V}_4\text{O}_{13}$ and $\text{Cr}_2\text{V}_4\text{O}_{13}$.

Mixtures: $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{V}_2\text{O}_5$, and $\text{Fe}_2\text{V}_4\text{O}_{13}/\text{Cr}_2\text{V}_4\text{O}_{13}$ weighed and homogenised by triturating were heated under conditions that would ensure to establish a state of equilibrium.

After each heating cycle the samples were examined by X-ray phase analysis. The equilibrium state was confirmed by comparing the results of two consecutive heating cycles. The results being identical, the equilibrium state was considered to be established, and the heating was terminated. The samples obtained after the final heating cycle were examined by the DTA method, too.

Samples comprising up to 60.00 mol% of $\text{Cr}_2\text{V}_4\text{O}_{13}$ in terms of components of the title system were heated until a state of equilibrium was established. The heating cycles were as follows: 873 K (24 h) \rightarrow 893 K (24 h) \rightarrow 903 K (24 h) – 908 K (4 h) \times 3.

Samples comprising over 60.00 mol% of $\text{Cr}_2\text{V}_4\text{O}_{13}$, were additionally heated at 913 K in six four-hour cycles.

Results and discussion

Table 1 shows phase composition of the samples obtained after the final heating cycle. X-ray phase analysis of the thermally treated samples, being in a state of equilibrium, shows them to be mono-phases. In addition to what has been noticed on diffraction patterns of samples after the final heating stage, with the increasing Cr₂V₄O₁₃ content of initial mixtures, the position of diffraction reflections characteristic of Fe₂V₄O₁₃ was shifting towards greater 2θ angles, that is, to reflections corresponding to shorter interplanar distances, *d*.

Table 1 Compositions of oxide initial mixtures and X-ray phase analysis of thermally-induced samples after the last heating cycle

Composition of initial mixtures/mol%			Mol% of Cr ₂ V ₄ O ₁₃ in mixture	Formula of the Fe _{2-x} Cr _x V ₄ O ₁₃ solution obtained
Fe ₂ O ₃	Cr ₂ O ₃	V ₂ O ₅		
30.00	3.33	66.67	10	Fe _{1.8} Cr _{0.2} V ₄ O ₁₃
26.67	6.66	66.67	20	Fe _{1.6} Cr _{0.4} V ₄ O ₁₃
23.33	10.17	66.67	30	Fe _{1.4} Cr _{0.6} V ₄ O ₁₃
20.00	13.33	66.67	40	Fe _{1.2} Cr _{0.8} V ₄ O ₁₃
16.67	16.66	66.67	50	FeCrV ₄ O ₁₃
13.33	20.00	66.67	60	Fe _{0.8} Cr _{1.2} V ₄ O ₁₃
10.00	23.33	66.67	70	Fe _{0.6} Cr _{1.4} V ₄ O ₁₃
6.67	26.66	66.67	80	Fe _{0.4} Cr _{1.6} V ₄ O ₁₃
3.33	30.00	66.67	90	Fe _{0.2} Cr _{1.8} V ₄ O ₁₃

The experimental results shown and those of indexing the X-ray powder diffraction pattern of the FeCrV₄O₁₃ thermally-induced monophase sample (REFINEMENT program) have shown that continuous solid solutions of a Fe_{2-x}Cr_xV₄O₁₃ type with a Fe₂V₄O₁₃ structure are formed in the Fe₂V₄O₁₃–Cr₂V₄O₁₃ system.

Table 2 shows parameters and volumes of unit cells of the Fe₂V₄O₁₃ [7] and Cr₂V₄O₁₃ compounds, as well as the FeCrV₄O₁₃ solid solution.

Table 2 Unit cell parameters and volumes for the Fe₂V₄O₁₃, Cr₂V₄O₁₃ and FeCrV₄O₁₃ solid solution

Formula	<i>a</i> /nm	<i>b</i> /nm	<i>c</i> /nm	β/°	<i>V</i> /nm ³
Fe ₂ V ₄ O ₁₃	0.8313(2)	0.9405(2)	1.4577(2)	102.23(2)	1.1138
FeCrV ₄ O ₁₃	0.8289(3)	0.9349(3)	1.4561(4)	102.45(2)	1.1013
Cr ₂ V ₄ O ₁₃	0.8270(3)	0.9303(3)	1.4552(4)	102.66(3)	1.0924

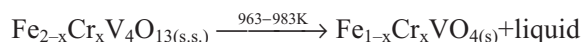
Analysis of the X-ray phase analysis results and the data tabulated in Table 2 has pointed out that with the increasing degree of Cr³⁺ ion incorporation into the Fe₂V₄O₁₃ lattice, a contraction of the solid solution crystal lattice follows; the measure of the contraction is a decreasing value of the unit cell volume. In other Fe_{2-x}Cr_xV₄O₁₃ solid

solutions, Fe³⁺ ions with an ionic radius equal to 64.5 pm are replaced by a successively larger number of Cr³⁺ ions, the ionic radius of which is smaller and amounts to 61 pm. The characteristics account for the contraction of the phase crystal lattices.

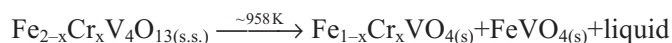
Two endothermic effects were recorded up to 1273 K on the DTA curves of samples comprising only a solid solution of Fe_{2-x}Cr_xV₄O₁₃, where 0.2 ≤ x ≤ 1.8. With the increasing degree of the Cr³⁺ ion incorporation into the Fe₂V₄O₁₃ lattice, the onset temperatures of the first and the second endothermic effects increased inconsiderably. The first effect started at a temperature range 953–1003 K whereas the onset temperature of the second effect was fluctuating between 1148 and 1178 K.

The temperature at which the first endothermic effect, recorded on DTA curves of all the final thermally treated samples, started at 953–1003 K – was considered as the temperature up to which the Fe_{2-x}Cr_xV₄O₁₃ solid solutions maintain thermodynamic stability. In order to support this assumption, two selected thermally-induced samples, comprising the phases, FeCrV₄O₁₃ (x=1) and Fe_{0.4}Cr_{1.6}V₄O₁₃ (x=1.6), were additionally heated at 933 K – at a temperature lower by ca 25 K of melting temperatures of the phases – then quenched to ambient temperature. Qualitative X-ray phase analysis of samples prepared in this way has proved that their phase composition remains unchanged, that is, they still contain FeCrV₄O₁₃ and Fe_{0.4}Cr_{1.6}V₄O₁₃ phases. On account of the isostructural character of the phases, Fe₂V₄O₁₃ and Cr₂V₄O₁₃, it is the Fe³⁺ ions that are incorporated into the structure of Cr₂V₄O₁₃ when samples contain over 50.00 mol% of Cr₂V₄O₁₃. The situation has been reflected in the X-ray phase analysis of samples heated at 933 K, indicating that a part replacement of Cr³⁺ ions by Fe³⁺ in the structure of Cr₂V₄O₁₃ raises the stability of the matrix which, as a pure compound, decomposes at 913 K.

In order to investigate the thermal stability of the solid solutions obtained, all monophasic samples containing Fe_{2-x}Cr_xV₄O₁₃ for 0.2 ≤ x ≤ 1.8 were additionally heated at 1038 K (3 h), that is, at a temperature close to the extremum of the first endothermic effect recorded on DTA curves. X-ray phase analysis of the melted and then quenched Fe_{2-x}Cr_xV₄O₁₃ solid solutions for 0.2 < x ≤ 1.2 has shown that they melt incongruently and the solid products of their melting are Fe_{1-x}Cr_xVO₄ phases [5]. The analysis of the position of reflections brought about by the samples shows that with the increase in the degree of the Cr³⁺ incorporation into the Fe₂V₄O₁₃ lattice, the degree of Cr³⁺ ion incorporation into the structure of Fe_{1-x}Cr_xVO₄ – the solid product of melting solid solutions – is increasing, too. The measured results have proved that the first endothermic effect, recorded on DTA curves of Fe_{2-x}Cr_xV₄O₁₃ solutions for 0.2 < x ≤ 1.2, is related with incongruent melting that can be written as follows:



X-ray phase analysis of other Fe_{2-x}Cr_xV₄O₁₃ solid solutions fused at 1038 K has shown for x ≤ 0.2 and x ≥ 1.4 that the solid products of their melting are Fe_{1-x}Cr_xVO₄ phases and FeVO₄ or CrVO₄, respectively. For example, the process of melting for Fe_{2-x}Cr_xV₄O₁₃ (x ≤ 0.2) can be written in the following way:



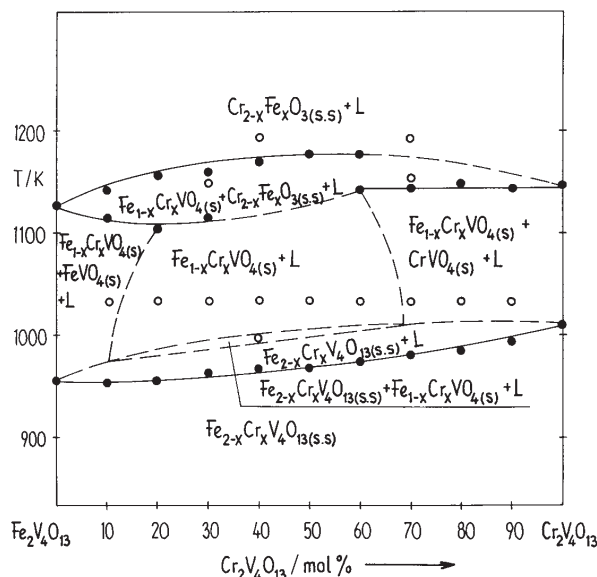


Fig. 1 The phase diagram of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ - $\text{Cr}_2\text{V}_4\text{O}_{13}$ system • – points indicate DTA, o – X-ray investigation after quenching samples in air

In order to ascertain that $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ is a solid product of melting $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ solid solutions for $0.2 < x < 1.2$, some samples representing that solubility range were heated at 1198 K (0.5 h), that is, at a maximum temperature of the second effect recorded on their DTA curves and then quenched. A qualitative phase analysis of samples melted at 1198 K has shown that they contain a $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$ solid solution and, among other things, V_2O_5 , which crystallizes from the liquid. According to published data, the solid solution resulting from the $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$ mixture is the solid product of melting $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ phases [4]. The process provides an additional evidence that the second endothermic effect on DTA curves results from melting of a solid product brought about by melting $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ phases, that is, $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$. Figure 1 shows a phase diagram of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ - $\text{Cr}_2\text{V}_4\text{O}_{13}$ system covering the whole component concentration range up to 1273 K. The compositions of samples additionally heated at 995, 1038 and 1198 K and then quenched have also been marked in this diagram.

Conclusions

1. Some continuous substitution solid solutions of a $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ type, bearing a structure of $\text{Fe}_2\text{V}_4\text{O}_{13}$, are formed in the $\text{Fe}_2\text{V}_4\text{O}_{13}$ - $\text{Cr}_2\text{V}_4\text{O}_{13}$ system.
2. With the increasing degree of the Cr^{3+} ion incorporation into the crystal lattice of $\text{Fe}_2\text{V}_4\text{O}_{13}$ a contraction of the crystal lattice of an arising solid solution takes place – reflected by the decrease in the volume of unit cells.

3. Solid solutions of a $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ type melt incongruently and their melting temperatures gradually increase with the increasing degree of the Cr^{3+} ion incorporation into the $\text{Fe}_2\text{V}_4\text{O}_{13}$ structure.

4. The solid products of incongruent melting of $\text{Fe}_{2-x}\text{Cr}_x\text{V}_4\text{O}_{13}$ solid solutions for $0.2 < x \leq 1.2$ is a $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ solid solution phase, and for $x \leq 0.2$ and $x \geq 1.4$ – $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ solid solution phases and FeVO_4 or CrVO_4 , respectively.

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