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Investigation of the real composition of the phase formed in the Fe_2O_3–V_2O_5–WO_3 system

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A new, previously unknown, phase that occurs in a three-component system of transition metal oxides, Fe_2O_3–V_2O_5–WO_3, has been obtained from a reaction taking place in the solid state. The phase with the molecular formula, $Fe_8V_{10}W_{16}O_{85}$, melts incongruently at 830 ± 5 °C.

1. Introduction

Three-component systems of transition metal oxides are interesting subjects of investigation, mainly because the oxide components of the systems and the compounds which may be formed. From a literature survey, it appears that the Fe_2O_3–V_2O_5–WO_3 system has not yet been refined and, before the initiation of our investigations [1, 2], no research had been undertaken on it.

A three-component system is built from three two-component systems, i.e. Fe_2O_3–V_2O_5, V_2O_5–WO_3 and Fe_2O_3–WO_3. The first of the systems, Fe_2O_3–V_2O_5, is well known, particularly, with respect to the phase equilibria established in it [3]. In that system, two compounds exist: $Fe_2V_4O_{13}$ and $FeVO_4$, melting incongruently at 665 ± 5 °C and 850 ± 5 °C, respectively [3]. Components of the system with a mol 5% Fe_2O_3 content form a eutectic mixture with a melting temperature of 615 ± 5 °C and a solid solution of Fe_2O_3 in V_2O_5 with a mol 3% solubility limit at the eutectic temperature [3].

Literature data pertaining to the second of the two-component systems, i.e. V_2O_5–WO_3, are scarce. Those available imply that the oxide mixture of the system heated in an air atmosphere admixed with oxygen does not form a chemical compound [4, 5], but only a solid solution of WO_3 in V_2O_5 with a mol 7% solubility limit [6, 7]. The components of the system also form a eutectic mixture melting at 670 °C with a composition given [5], as approaching pure V_2O_5.

It follows from the literature survey that in the third system, Fe_2O_3–WO_3, one compound, Fe_2WO_6, was formed above 800 °C, whose structure above 950 °C is reported [8, 9] to undergo monotropic transformation to yield a superstructure. The melting temperature of Fe_2WO_6, given by various authors, is 1165 °C [10], 1142 °C [11], 1130 °C [12, 13], respectively; same authors [10, 12, 13] defined the melting as incongruent, but no solid product of the melting process was traced. However, other authors [11] found that Fe_2WO_6 melts congruently.

In the three-component systems Fe_2O_3–V_2O_5–MoO_3, Cr_2O_3–V_2O_5–MoO_3 and Al_2O_3–V_2O_5–MoO_3 one type of compound was found to form, which involves all three oxides $FeVMoO_7$ [14], $CrVMoO_7$ [15] and $AlVMoO_7$ [16]. Studies on the Fe_2O_3–V_2O_5–WO_3 system were initiated to determine whether $FeVWO_7$ occurs in the system. Primary experiments did not prove the formation of a phase with such a composition. On the other hand, they did show that the diffraction pattern of a preparation obtained by prolonged heating of a mixture with an initial composition $Fe_2O_3 + V_2O_5 + 4WO_3$, contained exclusively a set of unidentified reflections, N. Accordingly, the molecular formula, $FeVW_2O_{10}$, has been attributed to the phase characterized by these reflections [2].

Some verifying studies on two of the two-component systems of the three-component system of interest, were also carried out. Studies have confirmed that the components of the V_2O_5–WO_3 system, heated in air up to 600 °C, remain inert towards each other and do not react to give a compound containing the two metals. It was also found that in the third of the two-component systems, Fe_2O_3–WO_3, only one compound occurs: Fe_2WO_6. However, other works dealing with synthesis of that compound show that iron(III) tungstate occurs not only in two, as has been hitherto believed, but in three polymorphic varieties which we have called α-, β-, and γ- [17]. The α- and γ-Fe_2WO_6 varieties correspond to the low- and high-temperature forms of Fe_2WO_6, described previously [8, 9, 13]. The new form, β-Fe_2WO_6, is formed while heating a mixture of oxides, Fe_2O_3 and WO_3, at 750–840 °C. The transition of β-Fe_2WO_6 into γ-Fe_2WO_6 leads to an enantiotropic polymorphic variety of reconstruction type. Previously [17], the Roentgen characteristics of β-Fe_2WO_6 were given its basic crystallographic parameters were obtained by indexing the powder diffraction pattern of the phase.

Analysis of the X-ray powder diffraction analysis of β-Fe_2WO_6 has shown that on the diffraction pattern of the phase, reflections previously assumed to be lines belonging to the set N, are always recorded, which we have defined as being characteristic of the $FeVW_2O_{10}$ phase. They are two diffraction lines ($d = 0.302$ and 0.276 nm) whose intensities were insignificant in the

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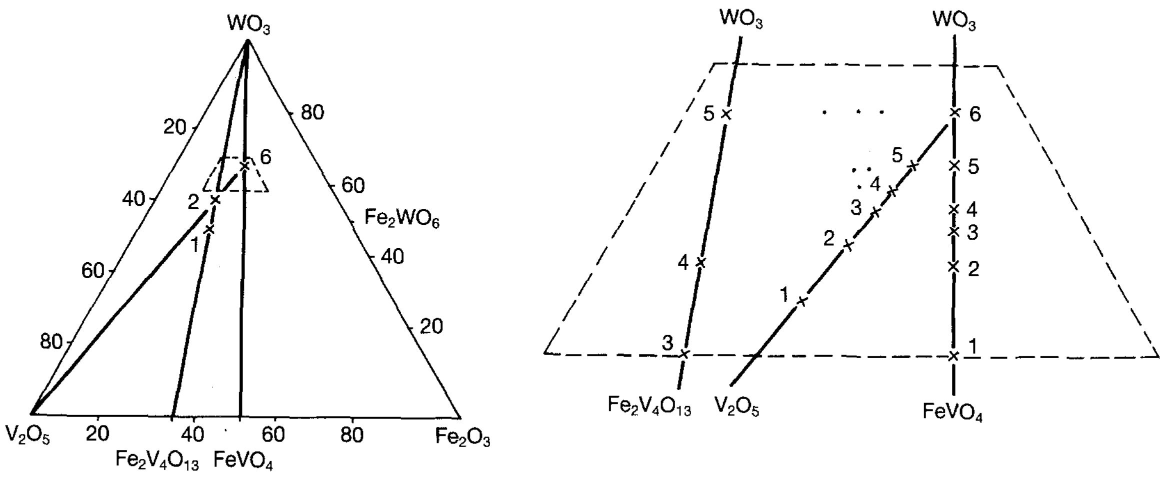

Figure 1 Positions on the component concentration triangle, of the samples investigated to determine the real composition of the phase formed in the Fe_2O_3–V_2O_5–WO_3 system.

set attributed to the $FeVW_2O_{10}$ phase. Works on the synthesis of β-Fe_2WO_6 have shown that they undoubtedly belong to the reflection set characterizing that variety, the reflections being of a much higher intensity. These lines cannot be acknowledged to be common to both reflection sets. This has stimulated further investigations of the composition of the phase characterized by the reflection set, N [2].

2. Experimental procedure

The following materials were used for the experiments: α-Fe_2O_3, p.a., prod. VEB (GDR), recalcined at 1000 °C within three 24 h cycles; V_2O_5, p.a., prod. POCh, Gliwice (Poland); WO_3, p.a., prod. Fluka AG (Switzerland), recalcined at 700 °C for 24 h; $FeVO_4$ and $Fe_2V_4O_{13}$, obtained by the technique described elsewhere [3]; and β-Fe_2WO_6 obtained by the method given in [17].

The samples were prepared for the experiments by weighing suitable oxides or compounds in the given proportions. After homogenization by powdering, the mixtures were pastilled and heated at the given temperatures within defined time cycles. After each stage of heating the preparations were cooled slowly to ambient temperature, then ground and subsequently subjected to X-ray phase powder diffraction and differential thermal analyses.

For the experiments, a number of preparations were prepared whose compositions are shown in Fig. 1. The synthesis was carried out by two methods: the preparations were heated in long cycles (24, 48, 72 and 120 h); or the heating time was much shorter, i.e. 3–6 h, the temperatures of the initial stages of heating being higher than those in the first method.

X-ray powder diffraction patterns were recorded using a Roentgen diffractometer DRON-3 with a CoK_α radiation and an iron filter. The phase composition of the preparations was refined based on data in the PDF charts [18, 19] and on those included in earlier publications [3, 13, 17].

DTA was made in air and quartz crucibles using a derivatograph J. Paulik-F. Paulik-L. Erdey, prod. MOM Budapest. All measurements were taken at 1000 ± 20 °C at a heating rate of $10\,°C\,min^{-1}$. The weight of 1000 mg was the same for all samples.

3. Results and discussion

Preparations of the first series, with compositions lying on the $FeVO_4$–WO_3 intersection (Fig. 1), were prepared either from the oxides (the components of the system under study) or from appropriate mixtures of $FeVO_4$ and WO_3. Preparations prepared from the oxides were heated under the following conditions

$$550\,°C\,(24\,h) + 600\,°C\,(48\,h) + 650\,°C\,(48\,h)$$
$$+\ 700\,°C\,(48\,h \times 3) + 720\,°C\,(48\,h \times 2 + 120\,h)$$

whereas the mixtures of $FeVO_4$ and WO_3 were heated as follows

$$700\,°C\,(48\,h \times 3) + 720\,°C\,(72\,h + 96\,h + 120\,h)$$

The initial mixtures made from oxides or $FeVO_4/WO_3$ mixture were also heated in short cycles

$$700\,°C\,(6\,h) + 720\,°C\,(6\,h \times 2)$$
$$+\ 725\,°C\,(6\,h \times 2 + 3\,h \times 2) + 735\,°C\,(3\,h \times 2)$$

X-ray phase powder diffraction analysis of the preparations prepared from oxides and heated in long cycles, after the first, the second and the third stage of heating, showed that the preparations were a mixture of $FeVO_4$ and WO_3. Not until the later stages of heating did the diffraction patterns of the preparations contain a set of unidentified lines, N, a set characteristic of β-Fe_2WO_6 [17] and, depending on the position of the sample on the $FeVO_4$–WO_3 intersection, lines typical of $FeVO_4$ or WO_3.

However, diffraction patterns of samples made from $FeVO_4$ and WO_3 also contained, immediately after the first stage of heating, the reflection sets characteristic of $FeVO_4$ and WO_3, lines N. After successive stages of heating, in addition to the set of lines N, lines typical of β-Fe_2WO_6 and, depending on the position of the sample on the $FeVO_4$–WO_3 intersection, a set of lines characteristic of $FeVO_4$ or WO_3.

X-ray diffraction patterns of preparations of that series showed after the final heating cycle that the

TABLE I The phase composition of preparations after the final heating cycle, with compositions lying on the $FeVO_4$–WO_3 intersection and obtained either from oxides or the $FeVO_4/WO_3$ mixture

Sample	Composition of initial mixtures in terms of the oxide content (mol %)			Phase composition[a]
	Fe_2O_3	V_2O_5	WO_3	
1	20.00	20.00	60.00	N, $FeVO_4$, β-Fe_2WO_6
2	18.75	18.75	62.50	N, β-Fe_2WO_6, $FeVO_4$ – traces
3	18.18	18.18	63.64	N, β-Fe_2WO_6
4	18.00	18.00	64.00	N, β-Fe_2WO_6
5	17.39	17.39	65.22	N, β-Fe_2WO_6
6	16.67	16.67	66.66	N, β-Fe_2WO_6, WO_3

[a] Shown in the sequence of decreasing content of individual phases. N, the set of unidentified reflection lines.

phase composition of individual preparations was not dependent on the type of substrates used to make the initial mixtures (Table I). On the other hand, changes in the phase composition of preparations heated in short cycles followed the other way round. Irrespective of the type of components used to prepare the initial mixtures, the diffraction patterns of the preparations after the first heating cycle showed, in addition to the set N, and the reflections characteristic of components of the initial mixtures, a few additional reflections, X, with a small intensity. The diffraction pattern of the preparations subjected to prolonged heating showed the intensity of lines N, to increase while the intensity of lines X, decreased until it faded. After the last heating cycle, the phase compositions of preparations obtained in this way were identical to those shown in Table I, except that β-Fe_2WO_6 was accompanied by α-Fe_2WO_6.

Irrespective of the method of synthesis applied, DTA, made after the last heating cycle of the samples, permitted either two or three endothermic effects to be found on the DTA curves of the samples. Accordingly, on the DTA curve of a preparation containing 60.00 mol % WO_3 in its initial mixture (Table I) three endothermic effects were recorded with peak onset temperatures of 780–790, 830–840 and 890–900 °C, respectively. However, on the DTA curves of other preparations of that series, only two endothermic effects were recorded with peak onset temperatures of 830–840 and 890–900 °C, respectively. The phase compositions of those preparations (see Table III below) imply that the effect with a peak onset temperature of 780–790 °C is caused by melting of a mixture that contains $FeVO_4$. The second effect (830–840 °C) has been assumed to result from incongruent melting of the phase under study, and the third one (890–900 °C), is bound by approaching the liquidus temperature. None the less, such an interpretation of the effects recorded on the DTA curve requires further experimental support.

Analysis of the phase composition of samples of that series (Table I) has shown that the molar ratio of iron(III) oxide to vanadium(V) oxide is lower than 1:1 in the phase under study. Based on that fact, some experiments were undertaken by preparing samples with compositions lying on the $Fe_2V_4O_{13}$–WO_3 intersection (Fig. 1), the molar ratio of α-Fe_2O_3 to V_2O_5 is 1:2 in that case.

Preparations of series 2 were also prepared from either oxides or the mixture $Fe_2V_4O_{13}/WO_3$, and heated under the conditions

$$550\,^\circ\mathrm{C}\,(24\,\mathrm{h}) + 600\,^\circ\mathrm{C}\,(48\,\mathrm{h}) + 615\,^\circ\mathrm{C}\,(72\,\mathrm{h} + 120\,\mathrm{h} \times 3) + 625\,^\circ\mathrm{C}\,(72\,\mathrm{h})$$

X-ray phase powder diffraction of the samples prepared from oxides, performed after the first two heating cycles, showed them to be a mixture of $FeVO_4$ and the initial components. The compositions of the preparations were becoming diversified after the subsequent heating cycles, that is, on the diffraction patterns of all the samples, lines N were accompanied by lines typical of V_2O_5 and, depending on the position of a preparation on the $Fe_2V_4O_{13}$–WO_3 intersection, by lines characteristic of $Fe_2V_4O_{13}$ or those belonging to WO_3. On the diffraction patterns of the samples obtained from some mixtures of $Fe_2V_4O_{13}$ and WO_3, the set N was visible just after the first heating cycle. Table II shows the phase compositions of preparations of series 2 after the final heating cycle.

TABLE II The phase composition of preparations after the final heating cycle, with compositions lying on the $Fe_2V_4O_{13}$–WO_3 intersection and obtained either from oxides or the $Fe_2V_4O_{13}/WO_3$ mixture

Sample	Composition of initial mixtures in terms of the oxide content (mol %)			Phase composition[a]
	Fe_2O_3	V_2O_5	WO_3	
1	16.67	33.33	50.00	N, $Fe_2V_4O_{13}$, V_2O_5
2	14.29	28.57	57.14	N, V_2O_5
3	13.13	26.67	60.00	N, V_2O_5, WO_3
4	12.50	25.00	62.50	N, WO_3, V_2O_5
5	11.11	22.22	66.67	N, WO_3, V_2O_5

[a] Shown in the sequence of decreasing content of individual phases. N, the set of unidentified reflection lines.

TABLE III The phase composition of preparations after the final heating cycle, with compositions lying on the V_2O_5–"N"(Fe_2O_3 + V_2O_5 + $4WO_3$ or $FeVO_4$ + $2WO_3$) intersection

Sample	Composition of initial mixtures in terms of the oxide content (mol %)			Phase composition[a]
	Fe_2O_3	V_2O_5	WO_3	
1	15.38	23.08	61.54	N, $FeVO_4$-traces
2	15.79	21.05	63.15	N, $FeVO_4$-traces
3	16.00	20.00	64.00	N
4	16.13	19.35	64.52	N, β-Fe_2WO_6 – traces
5	16.33	18.36	65.31	N, β-Fe_2WO_6 – traces
6	16.67	16.67	66.66	N, β-Fe_2WO_6, WO_3

[a] Shown in the sequence of decreasing content of individual phases. N, the set of unidentified reflection lines.

DTA of preparations of series 2, made after the final heating cycle, showed a number of endothermic effects recorded on the DTA curves. For example, on the DTA curve of a sample with a 50.00 mol% WO_3 content in its initial mixture, five endothermic effects were found with peak onset temperatures of 620–630, 695–700, 800–810, 830–840 and 880–980 °C, respectively, whereas on the DTA curve of sample containing 57.14 mol% WO_3, only three endothermic effects were recorded with peak onset temperatures of 620, 830–840 and 890 °C, respectively. On the DTA curves of other preparations of the series (Table II), four endothermic effects were observed with peak onset temperatures of 620, 830–840 and 890 °C, respectively. Analysis of the effects recorded on the DTA curves of samples of the second series and those of samples of the first series, as well as the phase compositions of those preparations, suggest that it is the melting of a mixture containing free V_2O_5 that is responsible for the first effect on the DTA curve (620 °C).

After the final heating cycle, X-ray phase powder diffraction of preparations of the second series, particularly the phase composition of sample 2 (Table II) which is exclusively a mixture of a phase characterized by the set N and V_2O_5 as well as the analysis of the effects recorded on the DTA curves of preparations of the first and second series, have indicated that in the ongoing investigations, the pseudobinary intersection of V_2O_5 and the phase characterized by the set N, to which we have ascribed a molecular formula, $FeVW_2O_{10}$, should be taken into consideration [2].

Preparations of series 3, were prepared mainly from oxides. The exception was a sample containing 64.00 mol% WO_3 in its initial mixture (Table III) which was prepared from a mixture of $FeVO_4$ and appropriate oxides, as well as from β-Fe_2WO_6 and appropriate oxides. The first two preparations of that series were heated exclusively in long cycles

$$600\,^{\circ}\mathrm{C}\ (24\ \mathrm{h}) + 620\,^{\circ}\mathrm{C}\ (48\ \mathrm{h} + 72\ \mathrm{h}) + 700\,^{\circ}\mathrm{C}\ (48\ \mathrm{h}) + 720\,^{\circ}\mathrm{C}\ (48\ \mathrm{h})$$

The other samples of the third series were heated both in long cycles, such as those in the case of the first two samples, and in short cycles

$$720\,^{\circ}\mathrm{C}\ (6\ \mathrm{h} \times 2) + 725\,^{\circ}\mathrm{C}\ (3\ \mathrm{h} \times 4) + 735\,^{\circ}\mathrm{C}\ (3\ \mathrm{h})$$

X-ray phase powder diffraction of preparations of the series showed that after the primary stages of heating, they were a mixture of $FeVO_4$ and oxides – the components of initial mixtures. On the diffraction patterns of preparations heated for a longer time, set N was recorded and, for most of the preparations of the series, lines characteristic of other phases were found to occur in the system of interest. On the other hand, the diffraction patterns of preparations of that series heated in short cycles after the primary stages of heating showed, in addition to set N and the reflection sets typical of other phases of the system under study, a few additional reflections, X, whose intensity decreased with progression of synthesis, until it faded. Finally, the phase composition of samples of the third series, after the final heating cycle also appeared to be independent of the preparation method (Table III).

Two or three endothermic effects were found on the DTA curves of preparations recorded after the last heating cycle. Thus, on the DTA curves of preparations containing 61.54 or 63.16 mol% WO_3 in their initial mixtures (Table III), three endothermic effects were recorded: the first, quite small and decreasing with increasing WO_3 content of a given preparation, with a peak onset temperature 620 °C, and two other effects with peak onset temperatures of 820–830 and 890–910 °C, respectively. On the DTA curves of other preparations of the series, only two endothermic effects were recorded with peak onset temperatures of 820–830 and 890–910 °C, respectively. Quite a small effect, starting at 620 °C, did not occur on the DTA curves of preparations containing 64.00 mol% WO_3, or more.

The Roentgen phase analysis results are shown in Table III. It is seen that on the diffraction pattern of a preparation with a content of 16.00 mol% Fe_2O_3, 20.00 mol% V_2O_5 and 64.00 mol% WO_3, i.e. $4Fe_2O_3 \cdot 5V_2O_5 \cdot 16WO_3$, only those reflections after the last heating cycle which were eventually attributed to a set characterizing the phase formed in the Fe_2O_3–V_2O_5–WO_3 system, occur. However, no effect occurred which we had assumed to be related to the melting of a mixture containing free V_2O_5 (620 °C). Thus, 20.00 mol% V_2O_5 is the maximum content of oxide in the initial mixture at which the effect fails to occur. Fig. 2 shows the DTA curves of preparations 1, 2 and 3 of the third series (Table III) after the final heating cycle. Fig. 2 implies that an increase in the V_2O_5 content only up to 1 mol% compared with that in preparation 3 (Table III) causes the 620 °C effect to appear on the DTA curve. However, Roentgen

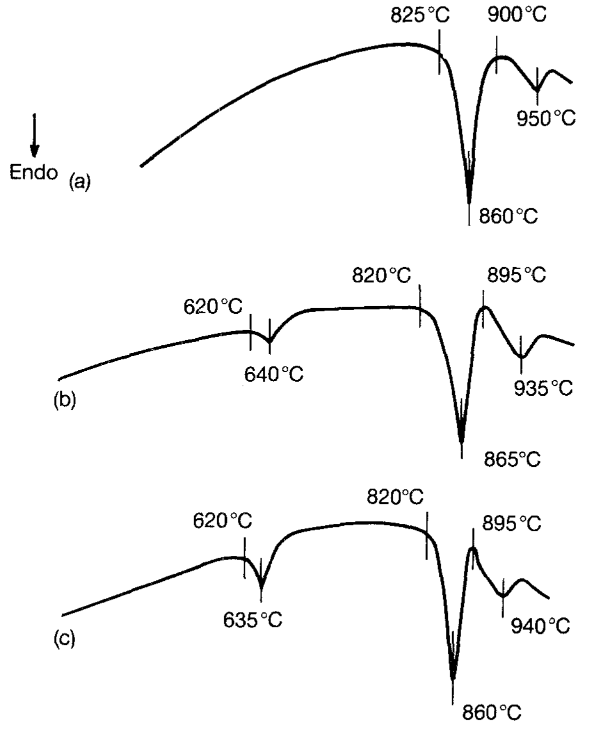

Figure 2 DTA curves of preparations (a) 1, (b) 2 and (c) 3 with compositions lying on the V_2O_5–"N" ($Fe_2O_3 \cdot V_2O_5 \cdot 4WO_3$) intersection after the final heating cycle.

analysis does not indicate the existence of V_2O_5 in preparations 1 or 2. Additional tests enabled us to establish that the occurrence of V_2O_5 in the preparations could not be confirmed by that method until the amounts reached 5 mol% V_2O_5.

The positions of other preparations investigated, i.e. those preparations not lying on the above-mentioned intersections, are also marked. The preparations were heated in long cycles. Roentgen analysis of the samples after the final heating cycle, showed in each case, the presence of a phase characterized by the set N, accompanied by reflections characterizing other phases. On the DTA curves of all the preparations after the last heating cycle three endothermic effects were recorded with peak onset temperatures of about 620, 820–840 and 890–910 °C, respectively, the first effect indicating an excess of V_2O_5.

The results presented of experiments carried out taking into account the existence of β-Fe_2WO_6 [17], are the basis for stating that in the Fe_2O_3–V_2O_5–WO_3 system, a phase exists in the formation of which all three oxides are involved; the phase had not been described prior to our studies. None the less, the molecular formula, $FeVW_2O_{10}$, previously proposed, is not applicable to this phase [2]. The results presented here prove that the phase involves about 3 mol% V_2O_5 more than originally thought. Thus, in the light of the experimental data presented, we can suggest that the molecular formula $Fe_8V_{10}W_{16}O_{85}$, the most adequate for the phase under study; it can also be written $8FeVW_2O_{10} \cdot V_2O_5$.

In order to support our viewpoint, and bearing in mind the objective of gaining an insight into the formation mechanism of the new phase and eventually refining the origin of reflections X, syntheses were performed by applying three different reactions taking place between substrates in the solid state

$$4Fe_2O_3 + 5V_2O_5 + 16WO_3 \longrightarrow Fe_8V_{10}W_{16}O_{85} \quad (1)$$

$$8FeVO_4 + V_2O_5 + 16WO_3 \longrightarrow Fe_8V_{10}W_{16}O_{85} \quad (2)$$

$$4Fe_2WO_6 + 5V_2O_5 + 12WO_3 \longrightarrow Fe_8V_{10}W_{16}O_{85} \quad (3)$$

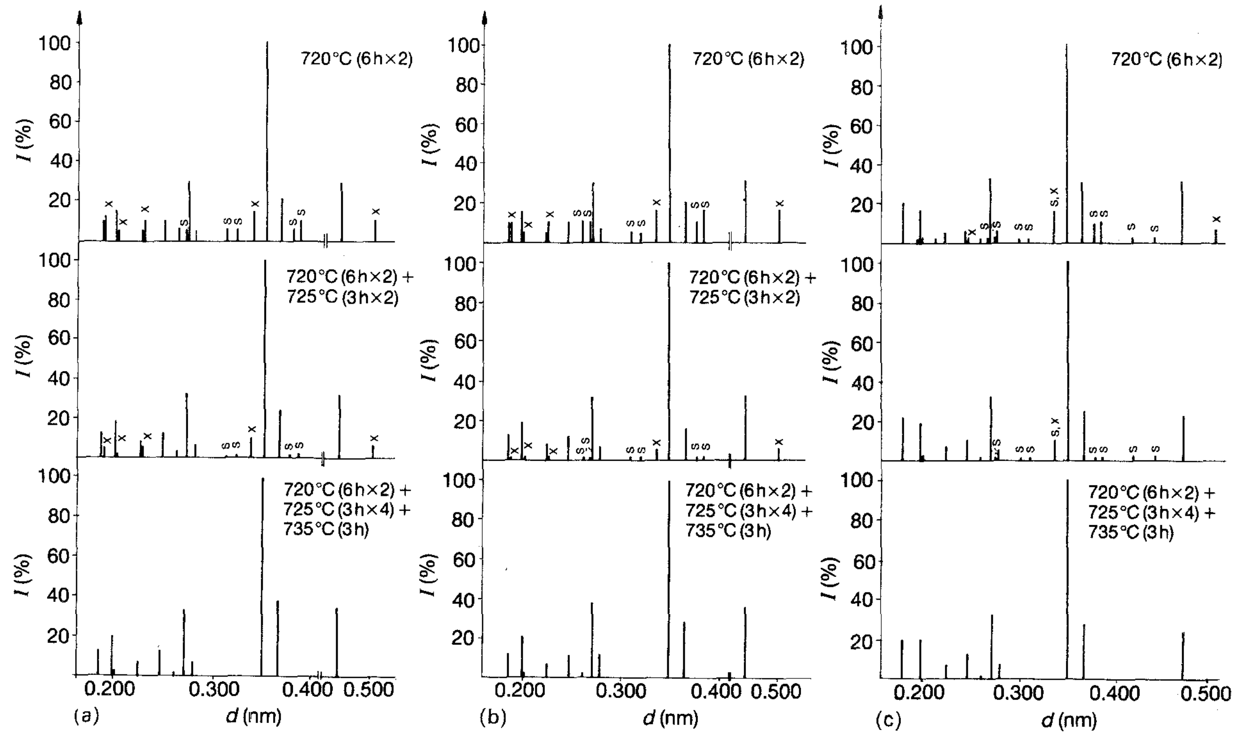

Figure 3 The course of synthesis of the phase formed in the Fe_2O_3–V_2O_5–WO_3 system according to Reactions 1–3, monitored by X-ray phase powder diffraction.

Synthesis was carried out identically in each case, by heating the samples under the conditions

$$720\,^{\circ}\mathrm{C}\,(6\ \mathrm{h}\times 2) + 725\,^{\circ}\mathrm{C}\,(3\ \mathrm{h}\times 4) + 735\,^{\circ}\mathrm{C}\,(3\ \mathrm{h}\times 2)$$

The course of the syntheses monitored by X-ray phase powder diffraction is shown in Fig. 3.

It follows from the data illustrated graphically that regardless of the initial composition of the mixtures, the diffraction patterns of the preparations exhibited the set N accompanied, after the primary stages of heating, by some additional lines, X, and lines typical of the substrates. As the synthesis progressed, a decrease in the line X intensity and in the lines typical of the substrates, took place until they faded. Thus a phase with the molecular formula $Fe_8V_{10}W_{16}O_{85}$, arises not only from oxides but also from $FeVO_4$ and Fe_2WO_6 reacting to completion, according to Equations 2 and 3. This was confirmed by DTA performed after the last heating cycle. It permitted us to determine that in all three cases, on the DTA curves only two endothermic effects had been recorded with peak onset temperatures of 825–835 and 890–900 °C, respectively (Fig. 2). Irrespective of the substrates used, the effect recorded at 620 °C and attributed to unreacted V_2O_5 was recorded for none of the samples under study.

No relation between the type of components used to prepare the initial mixtures and the additional lines, X, was noticed while the studies were in progress. It was only the time of synthesis that conditioned either the presence or absence of the lines during the course of synthesis. The previous studies do not allow their origin to be established unequivocally. However, they do imply that the synthesis of $Fe_8V_{10}W_{16}O_{85}$ takes place, yielding an unstable intermediate product with crystallites sufficiently well-shaped to cause the additional reflections characterizing the product to appear. Synthesis of the new phase carried out by prolonged heating of the substrates leads to decomposition of the product giving the final product of synthesis.

In order formally to confirm the correctness of the composition found for the phase under study, the product of the synthesis, assumed to be a monophase, was analysed for metallic components content. A specimen of the phase was fused with soda and then the melt was leached with water. After filtration, the precipitate was dissolved in hydrochloric acid and the iron content was determined by absorption spectroscopy [19]. The tungsten content in the filtrate was determined by the gravimetric method, to deposit the metal in the form of WO_3 using hydrochloric acid in the presence of cynchonine [20]. The vanadium content was determined by manganometric titration in a separate sample of the melt leached in sulphuric acid [20]. The analytical results (Fe 8.03%, V 9.69%, W 55.93%) are in a good agreement with the values calculated, based on the molecular formula of the phase, i.e. Fe 8.50%, V 9.69%, W 55.95%.

All the examinations accomplished by the DTA method have proved that $Fe_8V_{10}W_{16}O_{85}$ melts incongruently at 830 °C. In order to verify the melting method used, and to establish the type of phase or solid phases which are products of such a melting, a sample of the phase was heated for 24 h at 840 °C and then rapidly cooled. X-ray phase powder diffraction of the "frozen" melted product showed an absence lines N, characteristic of $Fe_8V_{10}W_{16}O_{85}$; only lines typical of WO_3 and α-Fe_2WO_6 were seen on the diffraction pattern. Thus, at $830 \pm 5\,^{\circ}\mathrm{C}$, the $Fe_8V_{10}W_{16}O_{85}$ phase melts incongruently by the following reaction

$$Fe_8V_{10}W_{16}O_{85(s)} \longrightarrow WO_{3(s)} + \alpha\text{-}Fe_2WO_{6(s)} + \text{liquid} \qquad (4)$$

Both WO_3 and iron(III) tungstate melt above 1000 °C and, consequently, the thermal effect associated with their melting cannot be seen on the DTA curves, it being visible only up to 1000 °C.

Contrary to all expectations, the results of the search for the real composition of the phase formed in the Fe_2O_3–V_2O_5–WO_3 system have shown that its composition does not correspond to $FeVO_4 \cdot 2WO_3$ [2]. The confirmation of the real formula of the phase in the formation of which all three oxides (the components of the interest) are involved, requires further study.

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