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Iron(III) tungstate and its modifications

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The conditions for the synthesis of Fe_2WO_6 in the solid state have been studied. It has been found that, at 750–840 °C, a new polymorphic modification can be obtained. Its X-ray diffraction characteristics are given and some of its properties determined.

1. Introduction

While studying the Fe_2O_3–V_2O_5–WO_3 system, we met difficulties in identifying, by X-ray powder diffraction, iron(III) tungstate, the sole compound of the Fe_2O_3–WO_3 system [1, 2]. The fact challenged us to undertake special investigations of the compound of interest and its modifications.

Fe_2WO_6 was obtained for the first time by Kozmanov from oxidation of ferberite above 600 °C, the author giving the X-ray diffraction characteristics of iron(III) tungstate as well [3]. The same data are applicable to a product from the oxidation reaction between iron oxides, namely Fe_2O_3, Fe_3O_4, wustite and WO_3 [3].

Bayer [4] obtained Fe_2WO_6 by heating an equimolar mixture of Fe_2O_3 and WO_3 at 760–850 °C for 20 h, and ascribed a columbite structure to the compound under study. According to Bayer, the product when heated for a fairly long time above 900 °C showed evolution of its structure, interpreted as the origination of superstructure. This coincided with the occurrence of several additional reflections in the diffraction pattern of Fe_2WO_6. According to Bayer [4] the lattice parameters for the unit cell of the superstructure are as follows: $a' = a$, $b' = 3b$ and $c' = 2c$, where a, b and c are the lattice parameters for the unit cell of Fe_2WO_6 with a columbite structure.

Trunov and Kovba [5] obtained Fe_2WO_6 by heating an equimolar mixture of Fe_2O_3 and WO_3 at 1000 °C for 70 h. They found that the Fe_2WO_6 obtained crystallizes in an orthorhombic system and belongs to one of the spatial groups Pnma or Pmmn, thus it is not isostructural with columbite.

However, it was Parant and his associates who carried out thorough studies on iron(III) tungstate [6]. They obtained two forms of Fe_2WO_6. Form I, called a low-temperature modification, was prepared by heating an equimolar mixture of oxides at 800 °C for 96 h. On the other hand, form II – a high-temperature modification – appeared as a product from the reaction of the same mixture of oxides heated instead at 900 °C for 48 h, then during a further 48 h at 950 °C. Heating of form I at a temperature higher than 900 °C led to form II. According to Parant *et al.* [6] the transformation observed is irreversible, and the relationship between the lattice parameters for the unit cell of form II and the parameters for form I can be shown to be as follows: $a' = a$, $b' = 3b$, $c' = 2c$. Hence the relation is consistent with that given by Bayer [4]. Like Bayer [4], Parant *et al.* [6] found the formation of form II concurrent with the appearance of a few additional reflections in the X-ray powder diffraction pattern of form I. On this basis, both Parant *et al.* and Bayer assented to a theory that form II is a superstructure developed from form I. Form I was defined by Parant *et al.* [6] as isostructural with columbite, whereas form II was assumed to be a stage in a likely transformation of a columbite–rutile type. Such a transformation of some crystal structures was conceived by other authors [7, 8].

Investigations designed to refine the crystal structure of Fe_2WO_6 were carried out by Senegas and Galy [9]. They obtained a pulverized preparation of Fe_2WO_6 by heating an equimolar mixture of Fe_2O_3 and WO_3 at 900 °C, obtaining a monocrystal of the compound of interest by using a method of chemical transport. The X-ray powder diffraction pattern of the iron(III) tungstate obtained proved consistent with that given by Trunov and Kovba [5].

A literature survey has shown that the state of studies on Fe_2WO_6 and its modifications is not satisfactory and unequivocal and requires further investigation. The literature survey furnished information on the existence of two forms of iron(III) tungstate, but the temperature range in which these forms exist was questionable. Accordingly, an investigation, intended to establish the temperature range and the conditions of heating under which a synthesis of the two Fe_2WO_6 forms is likely to take place, was launched. The other purpose of the investigation was to determine the types of transformation.

2. Experimental procedure

The following analytically pure reagents were used for experiments: α-Fe_2O_3 from VEB (GDR), heated additionally for 72 h at 1000 °C, and WO_3 from Fluka (Switzerland), heated for 48 h at 700 °C. A number of attempts were made to synthesise iron(III) tungstate by heating an equimolar mixture of Fe_2O_3 and WO_3

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for a given time and at a given temperature, the mixture being homogenized by grinding, then pastilled and heated.

X-ray powder diffraction of the preparations was made using an HZG 4/A-2 diffractometer (GDR), using CoK_α radiation and an Fe filter. Identification of the phases was made based on the data in PDF cards [10] and those found in publications [4–6, 9].

In addition, measurements were also made which consisted in directly tracing the course of the synthesis of iron (III) tungstate and formation of its modifications in a high-temperature X-ray chamber. We used a chamber of type UWD-2000 (USSR), placed on an HZG-4 goniometer. An equimolar mixture loaded in a nickel cuvette was placed in the chamber, heated to a given temperature and maintained in it for a given time, and then a diffraction pattern of the preparation was recorded under these conditions.

3. Results and discussion

Table I shows the results of the most representative trials of the iron (III) tungstate synthesis. They show that synthesis of the compound starts at a temperature as low as 650 °C. However, the rate of the synthesis under these conditions is quite low. A temperature increase to at least 750 °C gives only an insignificant increase in the reaction rate. It is only when the mixture is heated at 800 °C that the course of the synthesis of iron (III) tungstate is noticeable.

Following Parant *et al.* [6] in determining the Fe_2WO_6 modifications as form I and form II, it should be said that we never succeeded in obtaining form I in a pure form – this modification was always admixed with other components of the reaction mixture. Such difficulties were never encountered with form II of Fe_2WO_6.

Table I shows the experimental results from the study of the course of iron (III) tungstate synthesis. The results permit us to state unequivocally that a new set of reflections can be observed whenever the synthesis is being carried out at 750–800 °C, the reflections being ascribed to none of the two known forms of Fe_2WO_6 or to the initial oxides. This fact implies that Fe_2WO_6 also occurs in a third form, hitherto unknown, temporarily called form III of Fe_2WO_6.

Table II shows the X-ray diffraction characteristics of iron (III) tungstate given by different authors and based on our own measurements. The X-ray powder diffraction pattern of form I appears identical with those known from the literature survey. With form II, the observed difference in the relative intensities of some reflections compelled us to insert in Table II the literature data beside our own findings, so that the two kinds of data would be easy to collate. Table II shows also a new set of reflections attributable to form III.

Analysis of the data arranged in Table II permit us to state that form I lacks a reflection that could be ascribed exclusively to that form. The position of the most intensive diffraction line for form I is identical

TABLE I Synthesis of Fe_2WO_6

No.	Conditions of synthesis		Phase composition of preparation[a]
	Temperature (°C)	Time (h)	
1	550	24	Fe_2O_3, WO_3
	600	48	Fe_2O_3, WO_3
	650	48	Fe_2O_3, WO_3, Fe_2WO_6(I)–traces
	715	144	Fe_2O_3, WO_3, Fe_2WO_6(I)–a little
	800	24	Fe_2WO_6(I), Fe_2O_3, WO_3
	800	24	Fe_2WO_6(I), Fe_2WO_6(III)–traces
	950	24	Fe_2WO_6(II)
2	750	250	Fe_2WO_6(I), Fe_2O_3, WO_3
	750	240	Fe_2WO_6(I), Fe_2WO_6(III)
	750	72	Fe_2WO_6(III), Fe_2WO_6(I)
	900	12	Fe_2WO_6(III), Fe_2WO_6(I)–traces
3	800	144	Fe_2WO_6(I), Fe_2WO_6(III)–a little
	800	216	Fe_2WO_6(III), Fe_2WO_6(I)–traces
	850	72	Fe_2WO_6(III)
	950	96	Fe_2WO_6(III), Fe_2WO_6(II)
4	840	2	Fe_2WO_6(I), Fe_2O_3, WO_3
	840	24	Fe_2WO_6(II), Fe_2O_3, WO_3
	840	96	Fe_2WO_6(III), Fe_2WO_6(II)
	900	60	Fe_2WO_6(III), Fe_2WO_6(II)–traces
5	900	48	Fe_2WO_6(II)
	950	48	Fe_2WO_6(II)
	800	216	Fe_2WO_6(II), Fe_2WO_6(III)
6	800	4	Fe_2O_3, WO_3, Fe_2WO_6(I)
	800	12	Fe_2O_3, WO_3, Fe_2WO_6(I)
	800	3	Fe_2WO_6(I), Fe_2WO_6(III)–traces, Fe_2O_3–traces, WO_3–traces

[a] Phases arranged according to their decreasing contents in preparations.

TABLE II X-ray diffraction characteristics of Fe_2WO_6 according to different authors and to our own measurements

Form I			Form II								Form III	
Bayer [4]		Parant *et al.* [6]	Trunov and Kovba [5]		Parant *et al.* [6]	Senegas and Galy [9]		Our work				
d (nm)	*I* (%)	*d* (nm)	*d* (nm)	*I* (%)	*d* (nm)	*d* (nm)	*I* (%)	*d* (nm)	*I* (%)		*d* (nm)	*I* (%)
											0.746	46
											0.553	9
											0.480	1
			0.474	2								
					0.448							
			0.439	30	0.4395	0.442	16	0.441	29			
											0.438	27
			0.425	40		0.427	23	0.428	12			
			0.4175	20		0.418	8	0.4188	12			
											0.4155	25
											0.3727	31
0.356	48	0.354	0.3527	80	0.3541	0.3539	39	0.3539	53			
											0.3512	15
											0.3367	51
											0.3330	26
			0.3283	20	0.3301	0.3302	10	0.3300	7			
											0.3020	86
0.288	100	0.2882	0.2867	100	0.2886	0.2886	100	0.2883	100			
0.2785	12	0.2791	0.2782	40	0.2799	0.2791	7	0.2792	11			
											0.2763	64
											0.2730	16
			0.2691	20	0.2708	0.2703	8	0.2703	10			
											0.2501	24
0.2485	18	0.2484	0.2472	60	0.2491	0.2482	16	0.2483	11		0.2487	100
0.2430	23	0.2434	0.2424	60	0.2440	0.2433	24	0.2435	20			
											0.2396	38
											0.2297	15
			0.2363	2	0.2379	0.2372	4	0.2374	2			
0.2290	13	0.2289	0.2278	30	0.2294	0.2287	8	0.2289	18			
											0.2254	8
		0.2183	0.2174	20	0.2189	0.2183	4	0.2183	3		0.2182	20
					0.2170	0.2164	4	0.2164	5			
0.2150	8	0.2150	0.2155	20	0.2154	0.2149	5	0.2149	6		0.2153	6
			0.2128	10							0.2125	7
			0.2084	1				0.2090	1		0.2080	5
											0.2042	7
0.2036	11	0.2033			0.2038	0.2033	12	0.2037	10			
			0.2023	50	0.2022	0.2017	6	0.2021	10			
											0.2011	4
											0.2005	5
					0.1955	0.1949	4	0.1953	7		0.1957	2
			0.1941	30								
											0.1935	11
											0.1908	2
											0.1892	5
0.1860	7	0.1857	0.1848	40	0.1861	0.1855	5	0.1858	4			
						0.1829	4	0.1829	3			
			0.1820	20								
0.1780	5	0.1770	0.1763	30		0.1770	5	0.1772	5			
											0.1755	23
0.1720	15	0.1726	0.1717	60		0.1724	13	0.1728	20		0.1729	15
0.169	18										0.1694	13
											0.1688	36
		0.1683	0.1675	60		0.1683	16	0.1686	20		0.1685	32
0.167	22	0.1668				0.1667	25	0.1671	30		0.1666	9
			0.1660	80							0.1660	13

with that for form II. However, form III is basically different from both of the other forms in diffraction characteristics (Table II); moreover, its preparation in a pure form presents no difficulties.

Considering the X-ray diffraction characteristics of iron (III) tungstate one should attempt to elucidate the identification of both the forms under investigation (I and II). When synthesis is carried out up to and including 840 °C, form I is the first to arise, its characteristics corresponding to those shown in Table II. Further, prolonged heating of the reaction mixture at 750 or 800 °C leads to form III accompanied by form

I, and not by form II. The diffraction characteristics of form III are distinguishable from those of the other forms to such an extent that formation of form III can be proved conclusively. However, it is only when the temperature reaches 840 °C that a fairly long heating of the reaction mixture can give rise to the occurrence of form II of Fe_2WO_6 (beside form I). The formation of form II manifests itself through the occurrence in the diffraction pattern of several additional, not very intense reflections concurrent with those typical of form I. Form II is formed as well, as a first phase, directly from the oxides when the temperature is 900 °C. A decrease in the reaction temperature to 800 °C and a prolonged maintaining of that temperature account for a quantitative transformation of form II into form III. On the other hand, form III when heated at 950 °C for a longer time appears to be transformed completely into form II of Fe_2WO_6.

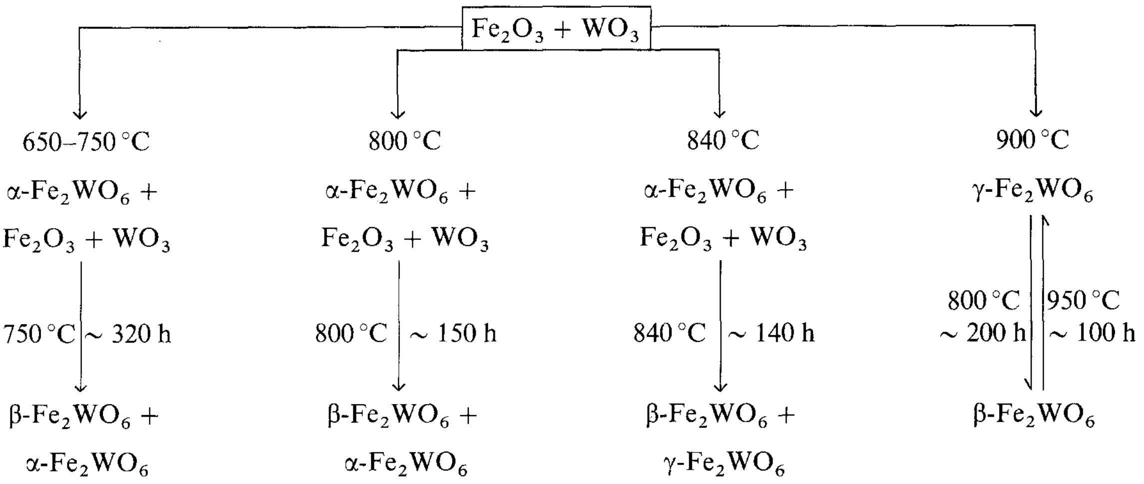
By denoting form I as α-Fe_2WO_6, form II as γ-Fe_2WO_6 and form III as β-Fe_2WO_6, the experimental results for the synthesis of iron(III) tungstate and its modifications can be presented in the form of a diagram.

Such a course of the synthesis of iron(III) tungstate at 650–950 °C has been confirmed by measurements made *in situ* using a high-temperature X-ray chamber.

The experimental results imply that the transformation of α-Fe_2WO_6 into β-Fe_2WO_6 is monotropic in character, since attempts to obtain the α-form from β-Fe_2WO_6 failed each time. However, the transformation of β-Fe_2WO_6 into a high-temperature modification, γ-Fe_2WO_6, shows the character of enantiotropic polymorphism. It is considered to be a transformation of a reconstruction type, the evidence of which is given by rather a small rate of the process and a wide range of temperature over which it can be observed.

TABLE III The results of indexing of the X-ray powder diffraction pattern of β-Fe_2WO_6

No.	d_{obs} (nm)	d_{calc} (nm)	hkl
1	0.746	0.7440	200
2	0.553	0.5536	001
3	0.480	0.4799	$20\bar{1}$
4	0.438	0.4394	110
5	0.4155	0.4161	201
6	0.3727	0.3732	400
7	0.3512	0.3517	$11\bar{1}$
8	0.3367	0.3371	111
9	0.3330	0.3331	$40\bar{1}$
10	0.3020	0.3021	$31\bar{1}$
11	0.2763	0.2762	311
12	0.2730	0.2730	$20\bar{2}$
13	0.2501	0.2504	510
14	0.2487	0.2488	600
15	0.2396	0.2396	$51\bar{1}$
16	0.2297	0.2297	112
17	0.2254	0.2255	$31\bar{2}$
18	0.2182	0.2182	511
19	0.2153	0.2153	601
20	0.2125	0.2123	021
21	0.2080	0.2080	402
22	0.2042	0.2042	312
23	0.2011	0.2012	221
24	0.2005	0.2004	$60\bar{2}$
25	0.1957	0.1957	420
26	0.1935	0.1934	710
27	0.1908	0.1908	$71\bar{1}$
28	0.1892	0.1892	$42\bar{1}$
29	0.1755	0.1754	711
30	0.1729	0.1728	$11\bar{3}$
31	0.1694	0.1694	801
32	0.1688	0.1688	620
33	0.1685	0.1685	222
34	0.1666	0.1666	$80\bar{2}$
35	0.1660	0.1660	$42\bar{2}$



The X-ray powder diffraction pattern of the β-Fe_2WO_6 phase obtained was subjected to indexing by two programs [11, 12]. The density of β-Fe_2WO_6 measured by the method described elsewhere [13] is 6.74 ± 0.05 g cm^{-3}. The results of indexing are shown in Table III. They dispose us to believe that β-Fe_2WO_6 crystallizes in a monoclinic system, and the parameters are $a = 1.5093$ nm, $b = 0.4597$ nm, $c = 0.5597$ nm, $\beta = 98.518°$. The number of molecules in the unit cell is $Z = 4$. The density calculated, $d_{calc} = 6.77$ g cm^{-3}, indicates good agreement with the value measured.

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