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INVESTIGATION ON THE THERMAL PROPERTIES OF $Fe_2O(SO_4)_2$

Part II

V. Petkova[1*] *and Y. Pelovski*[2**]

[1]Central Laboratory of Mineralogy and Cristallography, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bl. 107, 1113 Sofia, Bulgaria
[2]University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Str., 1756 Sofia, Bulgaria

Abstract

$Fe_2O(SO_4)_2$ is a secondary product of the decomposition of $FeSO_4{\cdot}H_2O$. Part I of this study presents results on the synthesis of $Fe_2O(SO_4)_2$ in gaseous environment containing either low or high concentration of oxygen. In this paper the existence of differences between the structures of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ is proved on the basis of a detailed thermal study of $Fe_2O(SO_4)_2$ upon dynamic heating (differential thermal analysis) and upon isothermal heating (thermal-analytic balance) in various gaseous environments as well as by presenting kinetic data on the processes of decomposition of both compounds.

Keywords: $Fe_2O(SO_4)_2$, $Fe_2(SO_4)_3$, kinetics, thermal decomposition

Introduction

The thermal decomposition of $FeSO_4{\cdot}H_2O$ in an oxidizing gaseous environment is characterized by the formation of $FeOHSO_4$ and/or $Fe_2O(SO_4)_2$ [1, 2]. In our previous investigations [3–5] it was proved that the formation of intermediate products, particularly of $Fe_2O(SO_4)_2$, depends mainly on temperature, the mode of heating and the ratio P_{H_2O}/P_{O_2}. In Part I of this study experimental data are presented on the synthesis of $Fe_2O(SO_4)_2$ when strictly controlling the parameters governing the process.

Another problem is the identification of $Fe_2O(SO_4)_2$ both as independent phase and mixed with other iron sulphates, e.g. $Fe_2(SO_4)_3$. These two compounds are characterized with very limited temperature regions of synthesis and decomposition and close Mössbauer spectroscopy and X-ray diffraction parameters [6–9].

The aim of this paper is a detailed thermal investigation of the mechanism and kinetics of decomposition of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ in air and in a gaseous environment containing $5.10^{-3}\%$ O_2+Ar gas well as demonstration of the differences in the structure of both compounds.

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[*] E-mail: vilma_bg@yahoo.com
[**] E-mail: pelovsky@uctm.edu

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Experimental

$FeSO_4 \cdot H_2O$ was used as starting material for synthesis of $Fe_2O(SO_4)_2$. Part I of this work describes in detail the composition and the characteristics of $FeSO_4 \cdot H_2O$ as well as the conditions for the formation of $Fe_2O(SO_4)_2$. In the present work we studied a product of the decomposition of $FeSO_4 \cdot H_2O$ for 30 min in pure oxygen upon isothermal heating at 813 K, the synthesis conditions for the formation being described in Part I [10]. To investigate thermal properties of $Fe_2(SO_4)_3$ we used as starting material chemically pure for analysis $Fe_2(SO_4)_3 \cdot 9H_2O$ (REACHIM) heated for 8 h at 593 K in order to obtain water-free $Fe_2(SO_4)_3$. X-ray diffraction and Mössbauer spectroscopy data for this material, studied experimentally later on, are presented in Figs 1a and 2 and in Table 1.

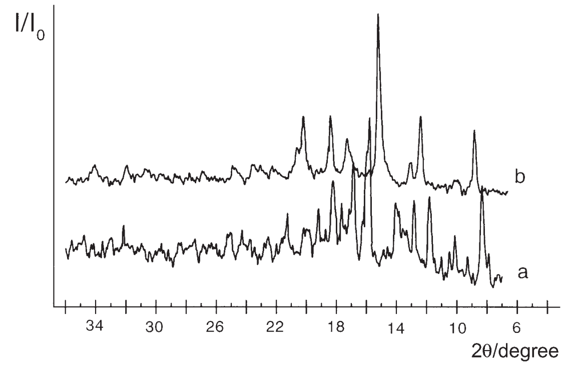

Fig. 1 X-ray diffraction patterns of: a – $Fe_2(SO_4)_3$ annealed at 593 K; b – $Fe_2O(SO_4)_2$ synthesized at 813 K

The thermal measurements carried out in air upon dynamic heating in the temperature range 293–1273 K were performed by a MOM derivatograph (Hungary) at a rate of 5 K min^{-1} using zircon crucibles of 8 mm diameter and 20 mm height. The measurements upon isothermal heating in a mixture $5 \cdot 10^{-3}$% O_2+Ar were carried out using a laboratory thermogravimetric equipment 'Shimadzu-31H' (Japan) with highly sensitive electronic thermal-balance, thermal-programming processor and register system. The sample mass was 50 mg, while the rate of the gas supply $1 \cdot 10^{-6}$ m^3 s^{-1}.

X-ray diffraction analyses were performed by a Philips apparatus using FeK_α radiation, while Mössbauer spectroscopy experiments by conventional equipment operating at a constant source (^{57}Co in Pd) acceleration calibrated with respect to α-Fe.

Results and discussion

The obtained experimental results are presented in Figs 1–5 and Tables 1–4.

As known [11, 12], difficulties exist when identifying $Fe_2O(SO_4)_2$ as intermediate product of the thermal decomposition of $FeSO_4 \cdot H_2O$ in oxygen. In spite of the numerous publications concerned with the formation of oxysulphate, the majority of authors have presented own results on the physical methods used for analyzing the pres-

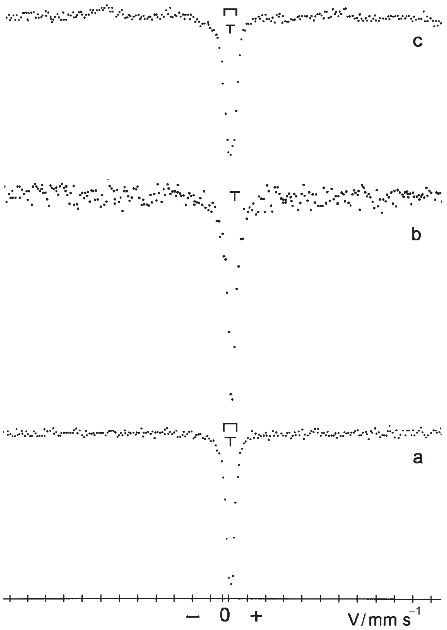

Fig. 2 Mössbauer spectra of a – $Fe_2(SO_4)_3$ annealed for 8 h at 593 K; b – $Fe_2O(SO_4)_2$ synthesized upon isothermal heating at 813 K in oxygen; c – $Fe_2(SO_4)_3$ obtained upon isothermal heating at 813 K in oxygen

ence of $Fe_2O(SO_4)_2$ [11, 12]. Usually, the unknown lines in the Mössbauer, X-ray diffraction and IR-absorption spectra have been related to those in the spectra of $Fe_2O(SO_4)_2$. Mössbauer spectroscopy, a precise physical method, also provides contradictory data on the isomeric displacement δ_{is} and the quadrupole splitting for ΔE_Q (Table 2).

Table 1 Mössbauer spectroscopy and X-ray diffraction data for the decomposition products of $FeSO_4{\cdot}H_2O$ and $Fe_2(SO_4)_3{\cdot}9H_2O$

T/K	Parameters		Contents of Fe^{n+}/%	Identifying phase	
	δ_{is}/ mm s^{-1}	ΔE_Q/ mm s^{-1}		Mössbauer spectroscopy	X-ray
593	0.50	–	81.0	$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$
	0.55	0.38	19.0	$Fe_2(SO_4)_3{\cdot}xH_2O$	$Fe_2(SO_4)_3{\cdot}3H_2O$
813	0.47	–	100.0	$Fe_2O(SO_4)_2$	$Fe_2O(SO_4)_2$
813	0.47	–	57.0	$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$
	0.50	0.38	43.0	$Fe_2(SO_4)_3{\cdot}xH_2O$	

Table 2 Mössbauer spectroscopic parameters for various iron sulphates

Compound	T/K	Parameters		Reference
		δ_{is}/mm s^{-1}	ΔE_Q/mm s^{-1}	
$Fe_2O(SO_4)_2$	298	0.425	1.439	[13]
		0.40–0.55	–	[3, 10]
	571	0.192	1.445	[14]
	646	0.156	1.416	[14]
	696	0.120	1.392	[14]
	733	0.760	–	[2]
	746	0.840	1.368	[14]
	793	0.730–	0.430–0.440	[2]
	–	0.740	1.40	[15]
		0.480		[15]
$Fe_2(SO_4)_3$	298	0.325–	0.330	[13]
	873	0.550	–	[2]
		0.380	–	[15]
		0.550–		[15]
		0.650		[15]
$Fe_2O(SO_4)_2{\cdot}xH_2O$	298	0.500	–	[3]
$Fe_2(SO_4)_3{\cdot}xH_2O$	298	0.500–	0.300	Own data
		0.550		Own data

In analyzing the data in Table 2 one can find that their values vary in a wide range, especially for $Fe_2O(SO_4)_2$. In addition, according to a part of the published data, the spectra of both sulphates consist of a single line, while according to others of a doublet. Most probably, this fact can be explained by the high hygroscopic capacity of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$, which as water-free compounds, generate a single spectral line, while, when absorbing moisture, form crystalline hydrates, thus enlarging the molecules of the corresponding sulphate, and, respectively, splitting its spectrum. This hypothesis is confirmed also by our results [3, 10], Table 1 and Fig. 2. To characterize more precisely $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ we are presenting the spectra of the solid products from the decomposition of $FeSO_4{\cdot}H_2O$ in oxygen at 813 K and that of $Fe_2(SO_4)_3{\cdot}xH_2O$ decomposed under the same conditions. In the former case $Fe_2O(SO_4)_2$ without impurities of other sulphates or oxides has been formed [10], while in the latter a product of the dehydration of $Fe_2(SO_4)_3{\cdot}xH_2O$, namely water-free $Fe_2(SO_4)_3$. This product reabsorbs moisture from air due to formation of new reactive surface (Fig. 2c). The experiments proved that upon thermal treating of $FeSO_4{\cdot}H_2O$ it decomposes forming $Fe_2O(SO_4)_2$, whereas $Fe_2(SO_4)_3{\cdot}xH_2O$ only dehydrates to form water-free $Fe_2(SO_4)_3$. The two compounds, especially when they do not contain impurities have the same Mössbauer spectral parameters (Table 1). This fact is reasonable, as the Mössbauer spectroscopy provides information correlating the distribution of valence electrons to that of Fe^{n+}. By analyzing the states of Fe^{3+} ions in $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ one can conclude that their coordination in both compounds is the same and this method is not appropriate to distinguish between them. So, other methods such as e.g. the thermal ones are required to prove the differences between the structures of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$. For the purpose we performed differential thermal analysis and the data are presented in Fig. 3 and Table 3.

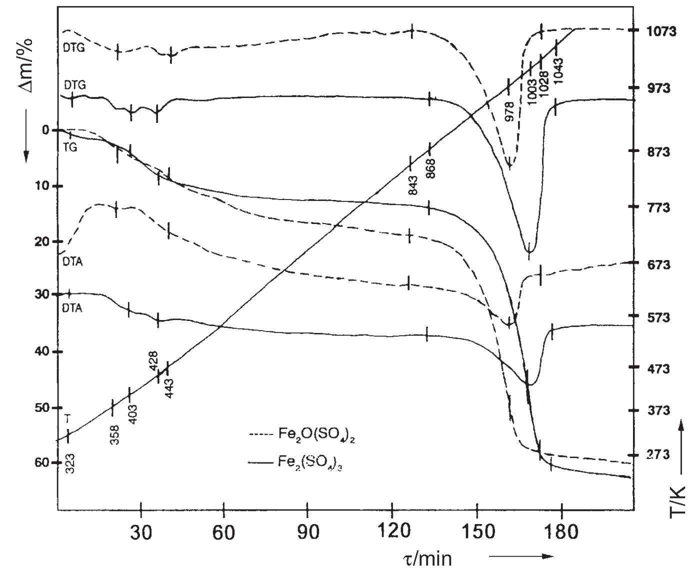

Fig. 3 TG-, DTG- and DTA-curves recorded during thermal decomposition of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ upon dynamic heating in air at a rate of 5 K min^{-1}

Table 3 TG-, DTG- and DTA data in the temperature ranges of transformation and losses of mass during thermal decomposition of dry $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$

Compound	Temperature range/K	Inflection temperature/K	Mass loss	
			Theoretical/%	Experimental/%
$Fe_2O(SO_4)_2$	843–1028	978	50.06	50.31
$Fe_2(SO_4)_3$	868–1043	1003	60.06	57.50

The mass loss during the thermal decomposition of $Fe_2O(SO_4)_2$ is calculated theoretically according to (1), while that of $Fe_2(SO_4)_3$ according to (2):

$$Fe_2O(SO_4)_2=Fe_2O_3+2SO_2+O_2 \tag{1}$$

$$Fe_2(SO_4)_3=Fe_2O_3+3SO_2+1.5O_2 \tag{2}$$

The TG, DTG- and DTA-dependencies obtained through differential thermal analysis of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ show that in the temperature range 353–443 K for both compounds the mass loss is between 9.5 and 11.1% due to re-hydration resulting from secondary absorption of air moisture during sampling, thus proving once more the high hygroscopic capacity of both compounds.

The main mass loss for $Fe_2O(SO_4)_2$ is in the temperature range 843–1028 K, while for $Fe_2(SO_4)_3$ between 868 and 1043 K, which can be explained by de-sulphurization of both compounds.

The decomposition of $Fe_2(SO_4)_3$ proceeds at temperatures about 20 K higher than those of $Fe_2O(SO_4)_2$, which proves the higher thermal stability of the former. The TG, DTG- and DTA-dependencies show that the desulphurization of both sulphates includes a single step without accompanying intermediate reactions, i.e. (1) and (2) describe best the destruction of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$. Consequently, the measured mass losses of 50.31% for $Fe_2O(SO_4)_2$ and of 57.50% for $Fe_2(SO_4)_3$ correspond to the stage of destruction of their structure and correlate with the theoretical values calculated according to (1) and (2). Just these differential thermal results confirm explicitly the thermal decomposition of two differing compounds. The difference of 10% theoretically calculated mass loss (7.21% by experiment) correlates with the fact that one SO_4^{2-} ion in the structure of $Fe_2(SO_4)_3$ is replaced by an oxygen atom in that of $Fe_2O(SO_4)_2$, which results in a difference of 10% between the mass losses. These results directly prove that at 813 K in oxygen we have produced namely $Fe_2O(SO_4)_2$, and the synthesis conditions used [10] are most appropriate for the formation of $Fe_2O(SO_4)_2$.

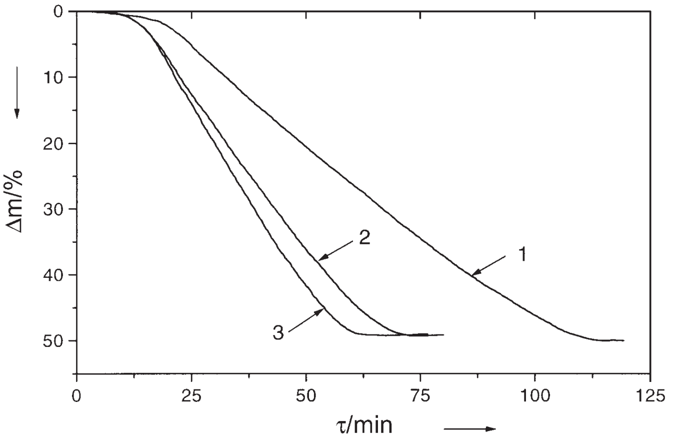

Fig. 4 Dependencies of the mass loss on the duration of decomposition of $Fe_2O(SO_4)_2$ in the temperature range 918–943 K in an environment of 5.10^{-3}% O_2+Ar. 1 – T=918 K; 2 – T=933 K; 3 – T=943 K

To confirm these results we performed experiments on the kinetics of thermal decomposition of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ in an environment of 5.10^{-3}% O_2+Ar and the data obtained are presented in Figs 4, 5 and Table 4.

The experimental kinetic data were processed using a computer program accounting for all widely used mathematical models for describing the possible solid state reactions. By fitting the experimental data to models using the least-square method we found that the results are best described through the Avrami equation with

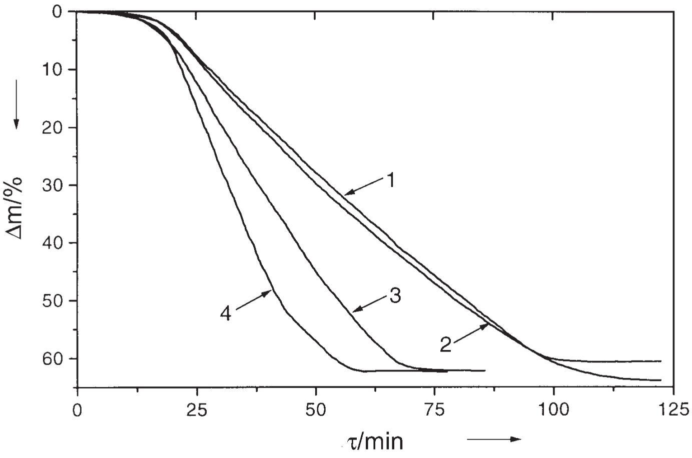

Fig. 5 The mass loss as a function of time for decomposition of $Fe_2(SO_4)_3$ in the temperature range 918–965 K in an environment of 5.10^{-3}% O_2+Ar. 1 – T=918 K; 2 – T=943 K; 3 – T=953 K; 4 – T=965 K

a power index n=3, which is typical of processes where the reaction products do not form on the whole sample surface. Most probably, in the beginning the decomposition develops into localized regions of the solid reagent and only then, in later stages, these reaction regions enlarge till the whole sample transforms into the final phase. This suggestion is confirmed also by the value of n. The kinetic analysis data discussed above and Figs 4 and 5 and Table 4 indicate that the structures of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ differs from one another.

Table 4 Data on the kinetics of thermal decomposition of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ at various temperatures in an environment of 5.10^{-3}% O_2+Ar

Compound	T/K	Mass loss/%	Kinetic equation	lgK_o	E/ kJ mol^{-1}	Correlation coefficient
$Fe_2O(SO_4)_2$	918	49.98	$kt=[\ln(1-\alpha)]^{1/3}$	5.866856	135.026	0.98048
	933	49.28				0.98820
	943	49.26				0.96232
$Fe_2(SO_4)_3$	918	63.85	$kt=[\ln(1-\alpha)]^{1/3}$	3.635232	96.473	0.98320
	943	60.44				0.98017
	953	62.22				0.99162
	965	60.12				0.99356

Conclusions

This investigation indicates the possibility for synthesizing $Fe_2O(SO_4)_2$ as a single-phase product from the thermal decomposition of $FeSO_4 \cdot H_2O$. New data are presented on the thermal stability and decomposition kinetics of $Fe_2O(SO_4)_2$ and

$Fe_2(SO_4)_3$ as the closest compounds in the systems studied. In combination, the results obtained in the course of this study, make it possible to control the thermal process in order to produce required final products.

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