Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 981–989

THERMAL AND STRUCTURE ANALYSIS OF $FeSO_4 \cdot H_2O$–BaO_2 MIXTURES

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

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

Abstract

Investigations on the thermal decomposition of $FeSO_4 \cdot H_2O$–BaO_2 mixtures were carried out under isothermal conditions by using simultaneously solid electrolyte cell (EMF-method). Evoked interactions producing oxygen in the temperature range 553–673 K were established by means of a solid electrolyte oxygen analyzer. Based on Mössbauer spectroscopy data and X-ray analysis it was proved that these reactions were associated with the release of oxygen from barium peroxide, oxidation of ferrosulphate–monohydrate to $FeOHSO_4$, and formation of barium ferrites such as $BaFe_2O_4$ and $BaFe_{12}O_{19}$.

Keywords: barium peroxide, iron(II)-sulphate, isothermal decomposition, oxygen measurements

Introduction

The mechanism of interactions in the system $FeSO_4 \cdot H_2O$–BaO_2 is of interest due to the possibility of some ferrites formation during the thermal decomposition process. Martinez–Tomayo *et al.* [1, 2] carried out experiments in inert gas environment. They determined compositions of reacted mixtures and obtained both of $BaFeO_3$ and Ba_2FeO_4. Pelovski *et al.* [3, 4] investigated interactions between $FeSO_4 \cdot H_2O$ and BaO_2 in gaseous environment and they fixed both the conditions and the initial mixtures, where the presence of $BaFe_2O_4$ and $BaFe_{12}O_{19}$ in solid reaction products were proved. Furthermore, they found that the formation of ferrite in the low temperature region started at 550–650 K, which was accompanied with intensive exothermal effects [5]. The basic feature of these interactions was the activity of atomic oxygen from BaO_2 and its high oxidizing effect. These reactions occurred in this temperature range of $FeSO_4 \cdot H_2O$ transformations and the possibilities of formation of intermediates as $FeOHSO_4$ and/or $Fe_2O(SO_4)_2$ [6–9].

The objective of this work is to investigate the mechanism of interactions between $FeSO_4 \cdot H_2O$ and BaO_2 in mixtures with molar ratios *n* from 1 to 4, in isothermal heating regime at 593–633 K and gaseous environment of standard mixture 1% H_2 and 99% Ar by means of a solid electrolyte oxygen analyzer.

---

* Author for correspondence: E-mail: vilma_bg@yahoo.com

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

$FeSO_4 \cdot 7H_2O$ and BaO_2 were chemically pure for analysis, supplied from RHEACHIM. The content of basic substance in the barium peroxide was 95.07%. $FeSO_4 \cdot 7H_2O$ was dehydrated to $FeSO_4 \cdot H_2O$ through preheating at temperature of 353 K and vacuum pressure of $0.6 \cdot 10^{-5}$ Pa. The product of dehydration contained 55.93% SO_4^{2-}, 34.57% Fe^{2+}, and 9.50% crystal water.

The end products of decomposition, as a different phases, were identified by X-ray diffraction and Mössbauer spectroscopy. Mössbauer analysis was carried out with standard Mössbauer spectrometer under constant acceleration of radioactivity source (^{57}Co in Pd). The calibration of the rate scale was given in respect of α-Fe. X-ray analyses were carried out with a DRON analyzer, radiation CoK_α.

The thermal investigations were carried out by laboratory device shown in Fig. 1.

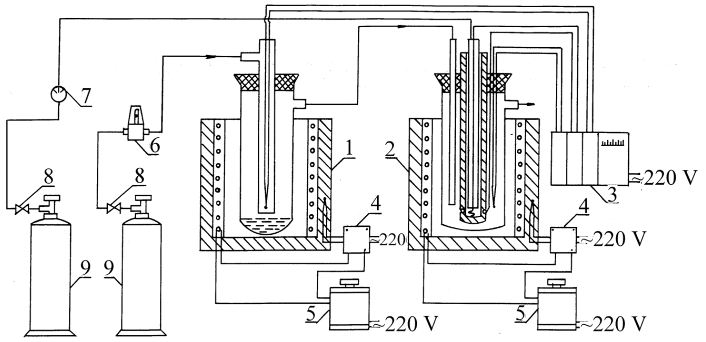

Fig. 1 Scheme of laboratory device for thermal treatment and determination of partial pressure of oxygen: 1 – furnace reactor; 2 – furnace with solid electrolyte; 3 – recorder; 4 – system for regulating temperature; 5 – adjustable resistor; 6 – rotameter; 7 – manometer; 8 – valve; 9 – containers with standard gas mixtures

This apparatus consists of temperature controlled electric furnaces. The former furnace is used for samples heated at given temperatures and the latter furnace is a part of the EMF cell for the determination a partial pressure of oxygen in the outlet gases from the first furnace.

The measurements are performed by the EMF method (determination of difference between partial pressures of oxygen, measured) using zirconium (ZrO_2) solid electrolyte stabilized by CaO and Y_2O_3. The oxygen temperature measurement is 1123 K. The reference electrode is placed in a pure oxygen atmosphere. The mass of samples is $1.0 \cdot 10^{-3}$ kg. The flow gas is standard mixture of 1% H_2 and 99% Ar with volume flowrate – 1.389×10^{-6} m^3 s^{-1} and pressure – $P_{O_2} = 3.16 \cdot 10^{-18}$ Pa.

Results

The results of the thermal decomposition studies of $FeSO_4 \cdot H_2O$–BaO_2 mixtures at different molar ratios are shown in Figs 2–6 and Table 1. Thermal decomposition of

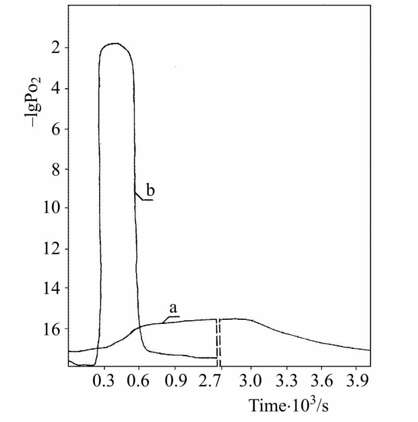

Fig. 2 The relationship between $-\lg P_{O_2}$ and time (s) at $T = 623$ K: a – $FeSO_4 \cdot H_2O$, b – mixture of Fe_2O_3 and BaO_2, $n = 12$

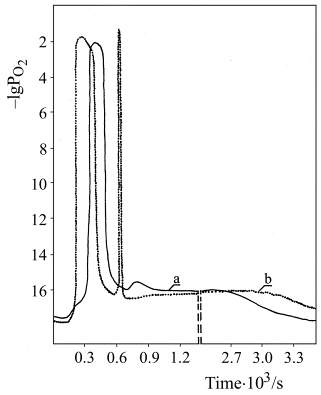

Fig. 3 The relationship between $-\lg P_{O_2}$ and time for $FeSO_4 \cdot H_2O$–BaO_2 mixtures, $n = 4$: a – $T = 593$ K, b – $T = 633$ K

$FeSO_4 \cdot H_2O$ and BaO_2 mixtures with molar ratios n=1–4 at oxidized gaseous environment and dynamic heating regime has proved [3–5] that the reactions at n=4 and n=2 have two stages with exothermal effects. In case of the reactions at n=1 the temperature range is very narrow –573–633 K and the decomposition is one-stage process. The investigations on the phase formation of $FeSO_4 \cdot H_2O$–BaO_2 systems, carried out both of dynamic heating [3, 4] and isothermal [5] regimes, determine that some barium ferrites such as $BaFeO_3$, $BaFe_2O_4$ and/or $BaFe_{12}O_{19}$ are obtained. These reactions are associated with exothermal effects registered. Furthermore, these reactions proceed with transport of oxygen, which is determined by registration of oxygen partial pressure changes with solid electrolyte measurements. For the pure $FeSO_4 \cdot H_2O$ at T=623 K the influence of treated time on the partial of oxygen is shown in Fig. 2a. After 360 s $\lg P_{O_2}$ increases 1.5 times –

from $-\lg P_{O_2}=17.06$ to $-\lg P_{O_2}=15.67$. Process time required is about $4.020\cdot 10^3$ s. When the process finished the content of oxygen in gaseous phase is fully restored. The Mössbauer spectrum of the decomposed solid product (Fig. 6, Table 1) is a combination of one doublet and straight line with $\delta_{is}=0.35\cdot 10^{-3}$ m s^{-1}. The double may be referred to $FeSO_4$ (91% Fe in sample) and straight line to $Fe_2O(SO_4)_2$ (Table 1) [8, 9].

Table 1 Mössbauer spectroscopy data for the solid products from thermal decomposition of $FeSO_4\cdot H_2O$–BaO_2 in 1% H_2 and 99% Ar and upon isothermal heating at T=623 K

No.	n	Parameters			Fe^{n+}	Content of Fe^{n+}/%	Phase identified by	
		$\delta_{is}/10^{-3}$ m s^{-1}	$\Delta E_Q/10^{-3}$ m s^{-1}	ΔH_{eff}/ kOe			Mössbauer spectroscopy	X-ray diffraction
1	–	1.27 0.35	2.80 –	– –	Fe^{2+} Fe^{3+}	91.0 9.0	$FeSO_4$ $Fe_2O(SO_4)_2$	–
2	4	1.27 0.45 0.40 –	2.82 1.42 0.20 –	– – 473.4 –	Fe^{2+} Fe^{3+} Fe^{3+} Fe^{3+}	74.0 20.0 4.0 2.0	$FeSO_4$ $FeOHSO_4$ $BaFe_2O_4$ $BaFe_{12}O_{19}$	$FeSO_4\cdot H_2O$, $BaSO_4$ $FeOHSO_4\cdot 2H_2O$, $BaFe_2O_4$, $BaFe_{12}O_{19}$
3	2	1.30 0.50 0.45 –	2.77 1.44 0.25 –	– – 472.0 –	Fe^{2+} Fe^{3+} Fe^{3+} Fe^{3+}	65.2 21.7 10.1 3.0	$FeSO_4$ $FeOHSO_4$ $BaFe_2O_4$ $BaFe_{12}O_{19}$	$FeSO_4\cdot H_2O$, $BaSO_4$ $FeOHSO_4\cdot 2H_2O$, $BaFe_2O_4$, $BaFe_{12}O_{19}$
4	1	1.30 0.40 0.40 –	2.80 1.40 0.20 –	– – 472.1 –	Fe^{2+} Fe^{3+} Fe^{3+} Fe^{3+}	69.4 15.8 11.8 4.0	$FeSO_4$ $FeOHSO_4$ $BaFe_2O_4$ $BaFe_{12}O_{19}$	$BaSO_4$, $FeOHSO_4\cdot 2H_2O$, $BaFe_2O_4$, $BaFe_{12}O_{19}$

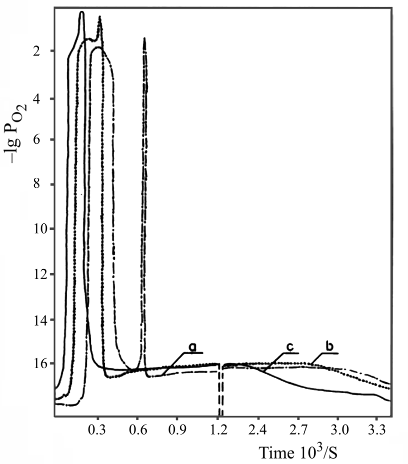

Fig. 4 The relationship between $-\lg P_{O_2}$ and time at T=623 K for $FeSO_4\cdot H_2O$–BaO_2 mixtures: a – n = 4, b – n = 2 and c – n = 1

The relationship between the partial pressure of oxygen (($\lg P_{O_2}$) and the mixing time at n=4 and T=593 K is shown in Fig. 3a. The same relationship at T=633 K is displayed in Fig. 3b. It is registered that from $2.4\cdot10^2$ s to $6.60\cdot10^2$ s after start of treating the partial pressure of oxygen significantly increases ($-\lg P_{O_2}$ =16.8–3.1). Obviously there are reactions in the system, in result of which the oxygen is evolved from gaseous medium. After the first peak the second low-area peak is registered after $6.60\cdot10^2$ s (Fig. 3a).

The amount of evolved oxygen expressed, as a relation between peak areas, increases up to 29 times. It is notable that the temperature rise from 593 to 633 K (Fig. 3b) is accompanied with changes of $-\lg P_{O_2}=f(\tau)$ relationship depended both on the time and the rate of process. The latter oxygen peak is more intensive and it is registered 120 s earlier (starts after 540 s and ends after 636 s). For this short period the $\lg P_{O_2}$ increase almost 14 times.

The $-\lg P_{O_2}=f(\tau)$ graphs at n=2 (or 1) and n=4 show that the most important differences observed are as follows: overlapping of the oxygen peaks, increasing of the registered peak areas (the amount of the released oxygen), and time decreasing for intensive oxygen releasing in the cases of the BaO_2 higher content in initial mixtures (Figs 3 and 4). We suppose that the higher process leads to formation of many origins, which cannot grow up under such conditions. This circumstance is confirmed by X-ray diffraction analysis. From X-ray diffractograms, shown in Fig. 5, it is determined that the peak intensity decreases, i.e. the structure of fine crystal products is formed as a result of rapid synthesis.

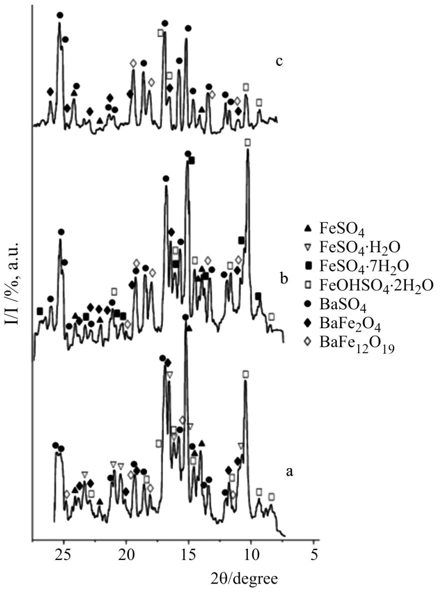

Fig. 5 X-Ray phase analysis of solid products from thermal decomposition of $FeSO_4\cdot H_2O–BaO_2$ mixtures at T = 623 K and gaseous environment of 1% H_2 and 99% Ar: a – n = 4, b – n = 2 and c – n = 1

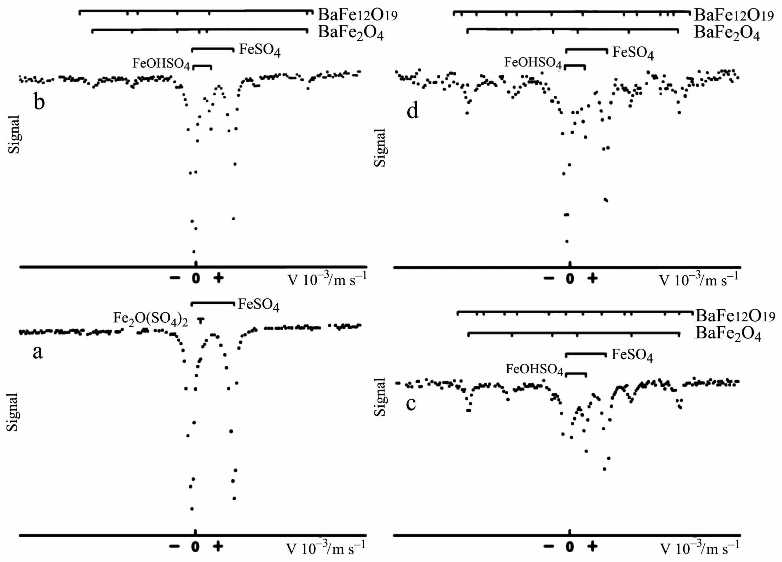

Fig. 6 Mössbauer spectroscopy of solid realized from thermal decomposition of $FeSO_4{\cdot}H_2O$–BaO_2 mixtures at $T = 623$ K and gaseous environment of 1% H_2 and 99% Ar: a – $n = 4$, b – $n = 2$ and c – $n = 1$

The quantity of obtained new phases as $FeSO_4$, $FeOHSO_4$, $BaSO_4$, $BaFe_2O_4$ and $BaFe_{12}O_{19}$ depends on the molar ratio between $FeSO_4{\cdot}H_2O$ and BaO_2. The X-ray diffraction show that the solid products obtained from decomposition of iron(II) and iron(III) sulphates are crystal hydrates because of air moisture absorption. The Mössbauer spectroscopy data (Fig. 6, Table 1) represent combination of two doublets and two sextets, where one of the sextets includes several under sextets. These are characteristic lines of $BaFe_{12}O_{19}$, identified by the clearest spectrum lines [4, 5]. The products of decomposition consist of 2–4% $BaFe_{12}O_{19}$ and it slightly increases when the content BaO_2 in mixtures is higher. The other sextet may be referred to $BaFe_2O_4$ and the doublets – to $FeSO_4{\cdot}H_2O$ and $FeOHSO_4$. The data show that the content of $FeSO_4$, evaluated by means of the samples content, is higher, but it decreases by 5–9% when the BaO_2 in initial mixtures is increased. From among other phases the intensity of $FeOHSO_4$ is the second. The content of Fe^{3+} in the form of $FeOHSO_4$ (δ_{is}=$0.45{\cdot}10^{-3}$ m s^{-1} and ΔE_Q=$1.42{\cdot}10^{-3}$ m s^{-1}) varies within the limits of 15–20% (Fig. 6, Table 1). The barium ferrites increase the content of Fe^{3+} in the form of $BaFe_2O_4$ is from 4% (for n=4) to 11.8% (for n=1).

The obtained data prove that at these experimental conditions used, the measured oxygen in the outlet gases is released from the reactions between mixture components. This is in a good agreement with the results from our previous investigations [3–5], namely the processes of ferrite formation and oxidation of $FeSO_4{\cdot}H_2O$ to $Fe_2O(SO_4)_2$, where the oxygen content plays an important role.

Discussion

On the basis of experimental results some suppositions may be proposed for the processes of oxidation of $FeSO_4·H_2O$ and that of ferrite formation in the $FeSO_4·H_2O–BaO_2$ mixture.

BaO_2

As was determined in our previous investigations [3–5], the reactions between components are initiated by releasing of atomic oxygen from structure of BaO_2 which can be described by the following reaction:

$$BaO_2=BaO+0.5O_2 \tag{1}$$

This process is accelerated by the presence of iron salts. As a result the initial decomposition temperature of BaO_2 is considerably lower. The $-\lg P_{O_2}=f(\tau)$ relationship for $Fe_2O_3–BaO_2$ mixtures shown in Fig. 2b proves these assumptions. For about 600 s the increase of $-\lg P_{O_2}$ value (–18.0–2) is registered. The released atomic oxygen causes reactions, which would be impossible in different conditions, such as barium ferrites formations even at T=623 K. These reactions are preceded very intensively. The solid products from barium component decomposition are distributed as $BaSO_4$ and barium ferrites.

Oxidation of $FeSO_4·H_2O$

Under experimental conditions used (isothermal heating regime at T=593–623 K and gaseous environment of mixture 1% H_2 and 99% Ar) the basic reactions is dehydration of $FeSO_4·H_2O$ to $FeSO_4$ (Figs 5 and 6, Table 1). Probably part of the released oxygen following reaction (1) is spent for oxidation of Fe^{2+} to Fe^{3+}. The data obtained from physical methods prove that the oxidation product in the mixtures with BaO_2 is $FeOHSO_4$ and in samples with pure $FeSO_4·H_2O$ is $Fe_2O(SO_4)_2$ (Figs 5 and 6, Table 1). In our previous investigations [6–9] it was proved that the formation of $FeOHSO_4$ and/or $Fe_2O(SO_4)_2$ the requisite temperature levels of P_{H_2O}/P_{O_2} in gaseous phase is needed. The equilibrium between the $FeOHSO_4$ and $Fe_2O(SO_4)_2$ is defined by the following reactions:

$$2FeSO_4·H_2O+0.5O_2=2FeOHSO_4+H_2O \tag{2}$$

$$2FeOHSO_4=Fe_2O(SO_4)_2+H_2O \tag{3}$$

The formation of $FeOHSO_4$ is determined under the temperature conditions: at 623 K, where $FeOHSO_4$ is a more stable phase than $Fe_2O(SO_4)_2$ [6, 8, 9]. The dehydration process sustains the necessary level of P_{H_2O}, and the level of P_{O_2} is sustained by the realization of atomic oxygen. We assume that with increase of the BaO_2 content in the initial mixture, the level of P_{O_2} increases, too. This leads to the formation of greater amounts of $FeOHSO_4$ (respectively smaller amounts of $FeSO_4$) for n=1–4. The content of iron in the form of $FeOHSO_4$ remains relatively stable: 15 to 20% for

n=1–4 (Table 1). Most probably $FeOHSO_4$ takes part in ferrites formation in the system. It is most likely that the registered amounts of $FeOHSO_4$ are residuum from these processes. It is supposed that namely $FeOHSO_4$ (from different iron sulphates $FeSO_4·H_2O$, $FeSO_4$ and $FeOHSO_4$) participates in the formation of barium ferrites, because of at T=623 K the $FeOHSO_4$ is less thermal stable than $FeSO_4$. At T=623 K and in the presence of atomic oxygen, it is most probable that the $FeOHSO_4$ interacts with BaO_2 at the least thermal stable of the iron sulphates. Otherwise, the $Fe_2O(SO_4)_2$ or $Fe_2(SO_4)_3$ should be involved in the synthesis reactions. Such phases were not registered by the physical methods applied.

The formation of $Fe_2O(SO_4)_2$ at heating of pure $FeSO_4·H_2O$ at T=623 K (Figs 2a, 6, Table 1) is an evidence that the equilibrium in reaction (3) is drawn out. The formation of $Fe_2O(SO_4)_2$ is more favorable, because the released water (as a vapor) is taken out of the system by the evolved gases at the initial stage. The oxidation of mixtures at T=623 K produces $FeOHSO_4$. Probably this is due to diffusion troubles caused from water released from the the samples surface. Thus the equilibrium in reaction (3) is drawn out to realization of $FeOHSO_4$.

Formation of ferrites

In our previous investigations [3–5] it was proved in the formation of ferrites in the system $FeSO_4·H_2O–BaO_2$ is initiated by releasing of atomic oxygen from the BaO_2 structure. The current investigations also prove that in the low temperature region it is possible to obtain some of them, namely $BaFe_2O_4$ and $BaFe_{12}O_{19}$. The formation of $BaFe_2O_4$ and $BaFe_{12}O_{19}$ proceed with evoked intensive exothermal reactions, where the oxygen is the product of reaction and the new phases are fine crystals (Fig. 5). The results shown in Figs 2–4, indisputably proves this fact. This determines the selection of gaseous environment (mixture of 1% H_2 and 99% Ar) to create sufficiently potential difference between the levels of oxygen partial pressure before and after the reactions of ferrites formation. On the basis of the obtained experimental results it is proposed the next most probable scheme of evoked reactions between $FeSO_4·H_2O$ and BaO_2 in mixtures with molar ratios n=1–4 at T=623 K and gaseous environment of 1% H_2 and 99% Ar.

$$BaO_2=BaO+0.5O_2 \tag{1}$$

$$2FeSO_4·H_2O+0.5O_2=2FeOHSO_4+H_2O \tag{2}$$

$$FeSO_4·H_2O=FeSO_4+H_2O \tag{4}$$

$$2FeSO_4+3BaO_2=BaFe_2O_4+2BaSO_4+O_2 \tag{5}$$

and/or

$$2FeOHSO_4+3BaO_2=BaFe_2O_4+2BaSO_4+H_2O+1.5O_2 \tag{6}$$

$$12FeOHSO_4+2BaO_2=BaFe_{12}O_{19}+BaSO_4+11SO_3+6H_2O+O_2 \tag{7}$$

$$BaO+SO_3=BaSO_4 \tag{8}$$

The evoked reaction (1) explains the registered first peak in relationships $-\lg P_{O_2} = f(\tau)$ (Figs 3a and 4) and the reactions (5) or (6) and (7) – the second one.

Conclusions

The obtained new data prove the possibility of barium ferrites formation in systems $FeSO_4 \cdot H_2O$–BaO_2 with molar ratios n=1–4 once again at different gas medium. The reactions are intensive and they evoked with the release of oxygen in gaseous phase and as a result the formation of $BaFe_2O_4$ and $BaFe_{12}O_{19}$ at T=623 K is proven. Unlike our previous studies, in the present investigations in the low-temperature range and gaseous environment of 1% H_2 and 99% Ar does not registered formation of $BaFeO_3$. The $BaFe_{12}O_{19}$ is formed in the high-temperature region only. These new data confirm for the first time small amount of $BaFe_{12}O_{19}$ at T=623 K. These results prove the important role of partial pressures of gaseous components on the phase compositions of solid products, obtained from thermal decomposition in $FeSO_4 \cdot H_2O$–BaO_2 mixtures with different molar ratios.

References

1 E. Martinez-Tomayo, A. Beltran-Porter and D. Beltran-Porter, Thermochim. Acta, 91 (1985) 249.
2 E. Martinez-Tomayo, A. Beltran-Porter and D. Beltran-Porter, Thermochim. Acta, 98 (1986) 167.
3 Y. Pelovski, V. Petkova, I. Dombalov and I. Gruncharov, J. Thermal Anal., 365 (1990) 1727.
4 Y. Pelovski and V. Petkova, Thermochim. Acta, 284 (1996) 407.
5 V. Petkova, J. Thermal Anal., 49 (1997) 1373.
6 Y. Pelovski, V. Petkova and S. Nikolov, Thermochim. Acta, 274 (1996) 273.
7 Y. Pelovski and V. Petkova, J. Thermal Anal., 49 (1997) 1227.
8 V. Petkova and Y. Pelovski, J. Therm. Anal. Cal., 64 (2001) 1025.
9 V. Petkova and Y. Pelovski, J. Therm. Anal. Cal., 64 (2001) 1037.