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Thermochemical decomposition of $FeSO_4 \cdot H_2O$–BaO_2 mixtures[1]

Y. Pelovski *, V. Petkova

Higher Institute of Chemical Technology, 8 "Kl. Ohridski" blvd.,
1756 Sofia, Bulgaria

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Abstract

The interactions in $FeSO_4 \cdot H_2O$(MhFS)/BaO_2 mixtures at molar ratios 0.5, 1, 2, 4 under oxidizing atmosphere and dynamic heating have been investigated with thermal, diffractometric and Mössbauer methods. The influence of temperature and partial pressure of the gaseous components on the rate of the process has been determined, as well as the formation of reaction intermediates such as $FeOHSO_4$ and $Fe_2O(SO_4)_2$. Process mechanisms are suggested for different molar ratios of the starting mixtures.

Keywords: Ferrites; $FeSO_4 \cdot H_2O$–BaO_2 mixtures; $FeSO_4 \cdot H_2O$(MhFS); Mössbauer spectroscopy; TG–DTA; X-ray diffraction

1. Introduction

The utilization of iron sulphate for the production of different ferrites is a new and promising trend for deep iron sulphate waste processing. In the literature there is only sketchy information concerning the synthesis of ferrites from $FeSO_4$ [1–3]. Martinez-Tomayo et al. studied the interactions between $FeSO_4$ and BaO_2 at different molar ratios in an inert gaseous medium [1] and reported that $BaFeO_3$ and Ba_2FeO_4 were obtained as end products. Pelovski et al. used a derivatograph to study the interactions occurring in the system MhFS–BaO–FeS_2 in an oxidizing gaseous medium [2, 3]. The

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* Corresponding author.

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solid phase products obtained were partly identified by X-ray analysis and Mössbauer spectroscopy.

The aim of the present work is to study the mechanism and interactions in the MhFS–BaO_2 system at molar ratios of $n = 0.5, 1, 2$ and 4 in an oxidizing gaseous medium and dynamic heating regime.

2. Experimental

The investigations have been performed in a dynamic heating regime at a rate $V = 5\ \mathrm{K\ min^{-1}}$ in the temperature range 293–1273 K using a MOM model Q1500-D derivatograph. The sample weight was 1000–1680 mg, the air flow-rate $25\ \mathrm{l\ h^{-1}}$. Zirconium crucibles with a internal diameter of 8 mm and height of 20 mm were used. The iron sulphate and barium peroxide were analytical reagent grade. The content of the main substance in BaO_2 was about 95.07%. When using the method of preliminary drying at a temperature of 353 K and vacuum of 0.6×10^{-5} Pa, the $FeSO_4 \cdot 7H_2O$ is mostly converted to MhFS. The dried product contains: 55.93% $SO_4{}^{2-}$, 34.57% Fe^{2+} and 9.50% water of crystallization. The intermediate and end products, resulting from the thermochemical decomposition were analyzed by Mössbauer spectroscopy and X-ray analysis.

The Mössbauer analyses have been carried out using a standard Mössbauer spectrometer, operating under constant acceleration of a radioactive source (^{57}Co in Pd). The calibration of the rate scale is given in relation to α-Fe.

3. Results and discussion

The derivatograms of the thermal processing of the preliminary prepared initial mixtures are presented in Figs. 1–4. The existence of BaO_2 in the samples significantly changes the mechanism and kinetics of the thermochemical decomposition of the iron sulphate [4].

From the TG curves it appears that the interactions that are taking place within the MhFS–BaO_2 system could be divided mainly into two stages. For the mixture of MhFS–BaO_2 with $n = 4$ (Fig. 1) the first stage takes place in the 553–663 K temperature range. It narrows with increasing quantities of BaO_2 in the system and at $n = 0.5$ and $n = 1$ it proceeds within the mentioned temperature range of 573–633 K (Figs. 3 and 4). This could be considered as an indication that the increased quantity of BaO_2 in the mixtures leads to intensification of the processes taking place during the first stage. On the basis of the TG-dependencies in Figs. 1 and 2 one could find two clearly defined stages, characterizing the parallel and consecutive proceeding of several reactions in the same temperature range of 553–663 K. For the first—at $n = 4$ and $T = 583$ K—weight losses of 4.0% were observed; for the second—at $T = 633$ K—the observed weight losses were about 1.4%. The total weight losses for the whole first stage at $n = 4$ were 7.3%. With the increased quantity of BaO_2 in the second stage the weight losses increase from 1.4% to 2.9% at $n = 2$, while the total losses are almost

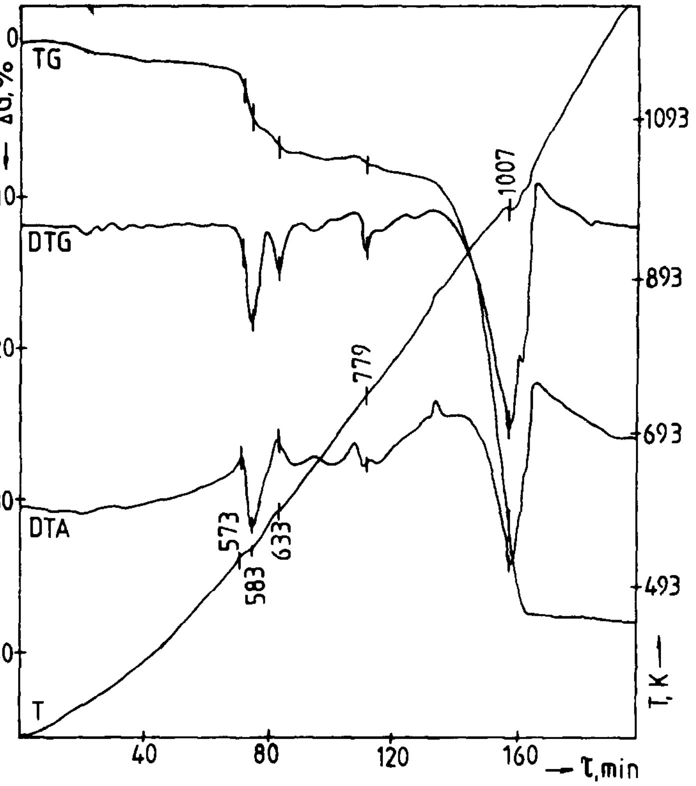

Fig. 1. A derivatogram of the thermal decomposition of the mixture with $n = 4$ at $V = 5\,\mathrm{K\,min^{-1}}$, in oxidizing gaseous medium and $G = 1000\,\mathrm{mg}$.

equal for both stages. At molar ratios of 1.0 and 0.5, the rate of the process occurring in this temperature range rises sharply. This leads to a single-stage progress of the interactions and the weight losses change by 5.5% in a period of just 1.0–1.5 min. Despite the increased content of BaO_2 in the mixtures the total weight losses for this stage remain almost constant—about 7.5%.

Two exothermal effects at 573 K and 633 K, separated by one endothermal peak at 583 K (Figs. 1 and 2) were apparent from the DTA-dependencies in the 553–673 K temperature range. With the increase of BaO_2 content in the samples (Figs. 3 and 4), the second exothermal effect appears at lower temperatures—613–623 K and is significantly more intense.

The data available from the literature [2, 3], as well as the experimental results obtained, suggest that the decomposition of the BaO_2 is activated primarily in the 553–613 K temperature range. The presence of iron in the samples strongly influences the course of the above-mentioned reactions. The evolving atomic oxygen is extremely reactive and acts on the monohydrate molecules. It is evident that this interaction leads to the formation of some quantities of ferrites and $BaSO_4$. The first exothermal effect at

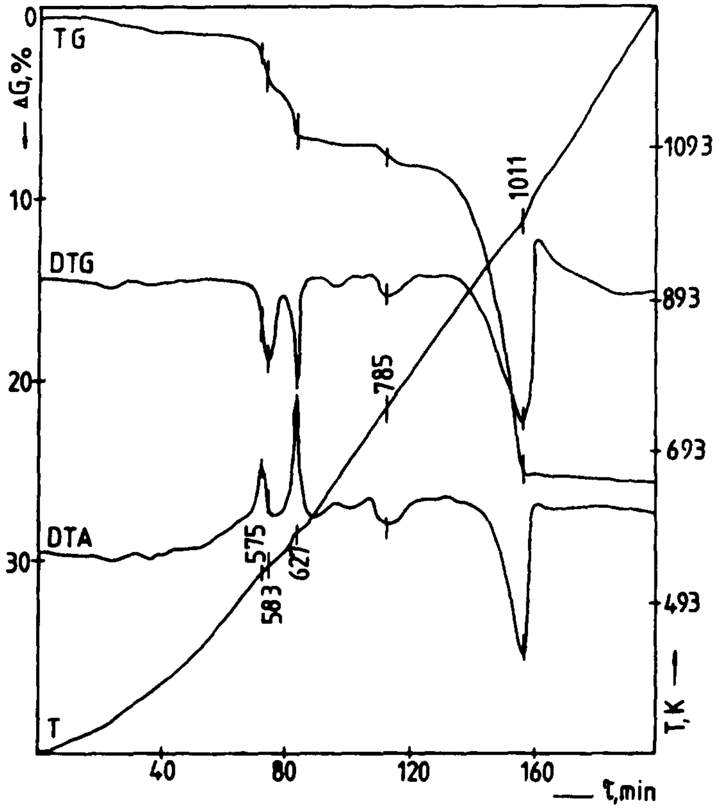

Fig. 2. A derivatogram of the thermal decomposition of the mixture with $n = 2$ at $V = 5\,\mathrm{K\,min^{-1}}$, in oxidizing gaseous medium and $G = 1210\,\mathrm{mg}$.

$T = 573\,\mathrm{K}$ is also assigned to this reaction. In this temperature range, a process of dehydration of part of the water of crystallization from the iron sulphate monohydrate also takes place. Evidence for this are the recorded weight losses of 4.0% and the endothermal effect at 583 K on the DTA curve—Fig. 1. In previous work [4], devoted to investigation of the thermochemical decomposition of MhFS in air, it was revealed that along with the dehydration another process of parallel oxidation of Fe^{2+} into Fe^{3+} was taking place, during which formation of hydroxy- and oxysulphates was observed. Samples containing greater MhFS content with molar ratios of $n = 2$ and $n = 4$ show changes analogous to those recorded during the thermal treatment of pure iron sulphate. The results obtained from the X-ray and Mössbauer spectroscopic analyses (Figs. 5a and 5b, and Table 1) confirm this coincidence in relation to the mechanism of interactions between MhFS and BaO_2 within the temperature range investigated.

On the basis of the X-ray spectra of the intermediate products obtained from decomposition of mixtures with $n = 4$ and $n = 2$, the existence of a mixture of $FeSO_4$,

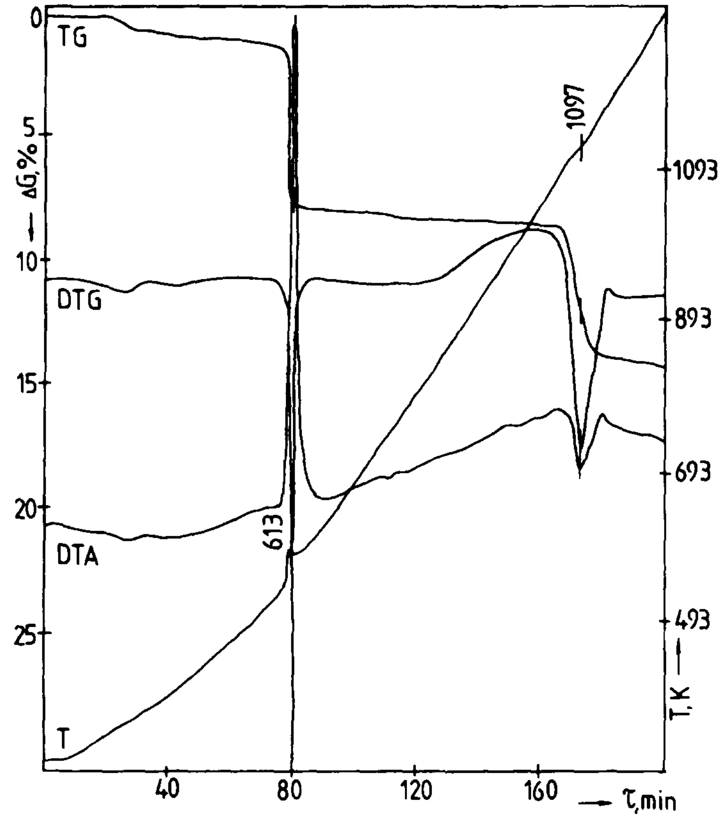

Fig. 3. A derivatogram of the thermal decomposition of the mixture with $n = 1$ at $V = 5\,\mathrm{K\,min^{-1}}$, in oxidizing gaseous medium and $G = 1628$ mg.

$FeOHSO_4$, $BaSO_4$ and $Fe_2O(SO_4)_2$ was established in the solid phase at temperatures up to 595 K and 605 K. The Mössbauer spectra of those samples present a combination of two doublets (Figs. 5a and 5b, Table 1). One split into a quarter and could be referred to as $FeSO_4$; the other as Fe^{3+}, i.e. $FeOHSO_4$. The results obtained coincide with those of Skeff Neto and Garg [5] and agree with data reported by other authors [6, 7]. In addition to the main doublets, the Mössbauer spectra prove the existence of small quantities of another phase; its spectrum presents a single band with isomeric shift of $0.4\,\mathrm{mm\,s^{-1}}$ and most probably it could be assigned to $Fe_2O(SO_4)_2$. At the base of one of the lines from the spectrum of $FeSO_4$ slight broadening was observed; this can be attributed to a comparatively weak doublet with $\delta_{is} = 0.3\,\mathrm{mm\,s^{-1}}$ and $E_Q = 0.5\,\mathrm{mm\,s^{-1}}$. This asymmetrical broadening could be explained by the existence of $BaFeO_3$ in the sample. The variations observed in the sample spectrum are presented more clearly in Fig. 5a, i.e. for $n = 2$.

On the basis of the analysis of the weight losses—1.4% and 2.9%—(Figs. 1 and 2) recorded in the 613–659 K temperature range, it could be assumed that they are

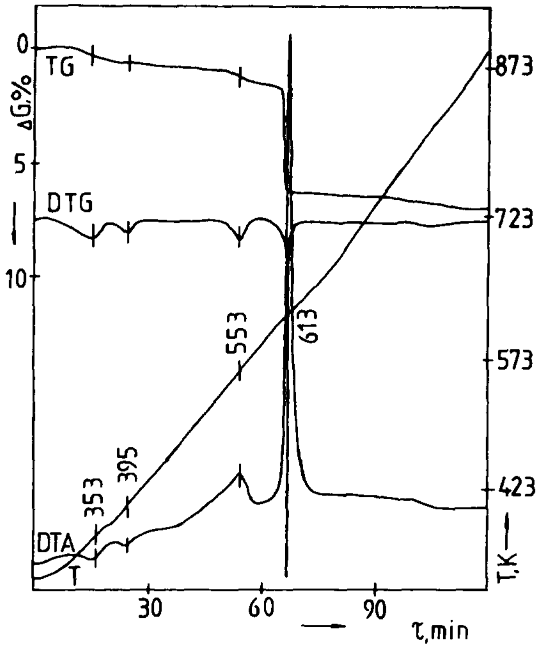

Fig. 4. A derivatogram of the thermal decomposition of the mixture with $n = 0.5$ at $V = 5\,\mathrm{K\,min^{-1}}$, in oxidizing gaseous medium and $G = 1000\,\mathrm{mg}$.

assigned to a continual exchanging reaction between the reagents and also to some restructuring of the solid phase. The DTA curves record this reaction by an exothermal effect at 627–633 K (Figs. 1 and 2). This assumption is confirmed also by the investigations carried out by the X-ray analysis (Table 1) and the Mössbauer spectroscopy (Fig. 5c). In accordance with the data obtained by those methods it can be stated that the solid product, obtained from decomposition of the mixture with $n = 2$ and Tup to 633 K, exhibits an altered crystal structure. Evidence for this is the reduction in intensity of the bands and the small increase in the halo on the X-ray pattern. Probably, the intense character of the interactions that are taking place leads to a formation of fine-grained crystal structure products. The Mössbauer spectra of the same sample (Fig. 5c) describe the products shown in Figs. 5a and b, but in this case the quantitative data show a decrease in the relative amount of $FeOHSO_4$ in the sample and a small increase in the oxysulphate. In addition to the spectra of these compounds, one could also observe a weak sextet, which proves the existence of magnetic phase in the smaple with intensity of the superfine magnetic field $H_{\mathrm{eff}} = 478\,\mathrm{kOe}$ and a quadruple split of $0.35\,\mathrm{mm\,s^{-1}}$. The latter is opposite in sign to that of Fe_2O_3 at room temperature. The characteristics of this sextet correspond to $BaFe_2O_4$ [8].

In accordance with the TG curves of the mixtures with molar ratios of $n = 2$ and $n = 4$ within the 779–785 K temperature range, the recorded weight losses were 1.2–2.3%. It is assumed that the $FeOHSO_4$ becomes more unstable at that temperature

Table 1
Mössbauer and X-ray data for intermediate and final products after thermochemical decomposition of $FeSO_4 \cdot H_2O$–BaO_2 mixtures

No	Temperature/K	n	Parameters			Valency Fe^{n+}	Content Fe^{n+}/%	Phases identified by:	
			δ_{is}/ (mm s^{-1})	ΔE_Q/ (mm s^{-1})	H_{eff}/kOe			Mössbauer spectroscopy	X-ray analysis
1	595	2	1.27	2.80	–	Fe^{2+}	21	$FeSO_4$	$FeSO_4$, $FeOHSO_4$,
			0.50	1.46	–	Fe^{3+}	71	$FeOHSO_4$	$Fe_2O(SO_4)_2$,
			0.40	–	–	Fe^{3+}	5	$Fe_2O(SO_4)_2$	$BaSO_4$
			0.30	0.50	–	Fe^{3+}	3	$BaFeO_3$	
2	605	4	1.27	2.75	–	Fe^{2+}	31	$FeSO_4$	$FeSO_4$, $FeOHSO_4$
			0.42	1.43	–	Fe^{3+}	62	$FeOHSO_4$	$Fe_2O(SO_4)_2$,
			0.48	–	–	Fe^{3+}	5	$Fe_2O(SO_4)_2$	$BaSO_4$
			0.30	0.50	–	Fe^{3+}	3	$BaFeO_3$	
3	663	2	1.27	2.75	–	Fe^{2+}	21	$FeSO_4$	$FeSO_4$, $FeOHSO_4$,
			0.42	1.43	–	Fe^{3+}	60	$FeOHSO_4$	$Fe_2O(SO_4)_2$,
			0.18	0.30	478	Fe^{3+}	11	$BaFe_2O_4$	$BaSO_4$
			0.50	–	–	Fe^{3+}	8	$Fe_2O(SO_4)_2$	
4	793	4	0.41	–	–	Fe^{3+}	70	$Fe_2O(SO_4)_2$	$Fe_2O(SO_4)_2$,
			0.40	0.42	516	Fe^{3+}	10	α-Fe_2O_3	$BaFeO_3$,
			0.42	1.40	–	Fe^{3+}	15	$FeOHSO_4$	$BaSO_4$
			0.20	0.45	–	Fe^{3+}	5	$BaFeO_3$	
5	1273	4	0.40	0.42	516	Fe^{3+}	94	α-Fe_2O_3	α-Fe_2O_3,
						Fe^{3+}	2–3	$BaFe_2O_4$	$BaSO_4$
						Fe^{3+}	3	$BaFe_{12}O_{19}$	
6	1273	2	0.40	0.42	516	Fe^{3+}	58	α-Fe_2O_3	α-Fe_2O_3,
			0.18	0.35	478	Fe^{3+}	22	$BaFe_2O_4$	$BaFe_2O_4$,
						Fe^{3+}	20	$BaFe_{12}O_{19}$	$BaSO_4$
7	1273	1	0.40	0.42	516	Fe^{3+}	46	α-Fe_2O_3	α-Fe_2O_3,
			0.18	0.36	478	Fe^{3+}	36	$BaFe_2O_4$	$BaFe_2O_4$,
						Fe^{3+}	18	$BaFe_{12}O_{19}$	$BaSO_4$
8	1273	0.5	0.10	0.60	–	Fe^{3+}	100	$BaFeO_3$	$BaFeO_3$,
									$BaSO_4$

and decomposes to $Fe_2O(SO_4)_2$. The X-ray pattern of the solid product, derived from decomposition of mixture with $n = 4$ and T up to 793 K, reveals the existence of $BaSO_4$, $FeSO_4$ and $Fe_2O(SO_4)_2$ with clearly apparent amorphization of the sample. The Mössbauer spectrum (Fig. 5d) shows the presence of certain quantities of $FeOHSO_4$—still not decomposed—and also Fe_2O_3.

For the mixtures with $n = 1$ and 0.5 (Figs. 3 and 4) it is assumed that the fast on-going reactions in the temperature range 613–633 K result in swift temperature increase. This may lead to a complete dehydration of MhFS to $FeSO_4$ without partial oxidation to $FeOHSO_4$ or $Fe_2O(SO_4)_2$. Those assumptions are confirmed by the lack of weight losses in the TG curves for the mixtures, shown in Figs. 3 and 4 in the temperature range 779–785 K. Therefore, the mechanism of those processes does not influence the formation of intermediates, such as $FeOHSO_4$ and $Fe_2O(SO_4)_2$.

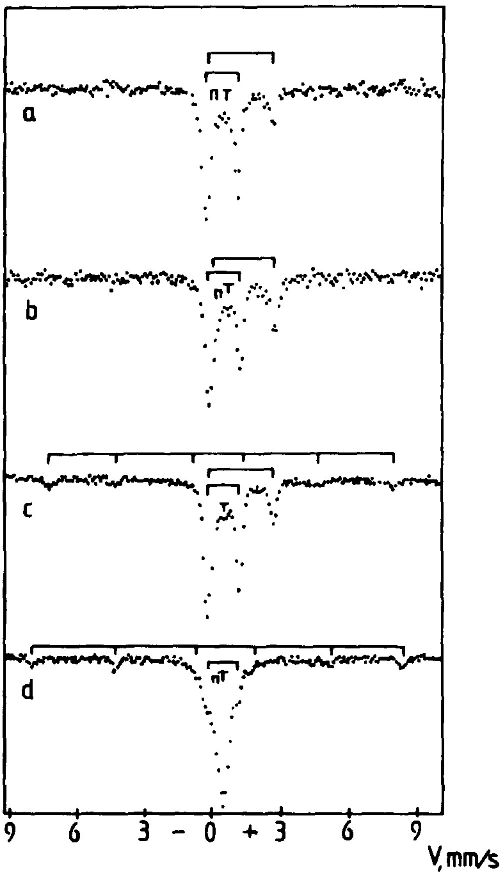

Fig. 5. Mössbauer spectra of the solid products from the thermal decomposition at $V = 5\ \mathrm{K\ min^{-1}}$ of: a) the mixture with $n = 2$ and $T = 595$ K; b) the mixture with $n = 4$ and $T = 605$ K; c) the mixture with $n = 2$ and $T = 663$ K; d) the mixture with $n = 4$ and $T = 793$ K.

Within the temperature range 883–1173 K weight losses, attributed to iron sulphate desulphurization, have been recorded. They significantly decrease with increasing amounts of BaO_2 in the mixtures. Thus, while for the molar ratio of $n = 4$ the recorded weight losses were about 28.6%, for $n = 0.5$ no weight losses were reported within the 883–1173 K temperature range; i.e. no excess of iron sulphate has been observed in the system. For $n = 4$ the process of desulphurization is shifted from 883–1063 K towards the higher temperature range of 1053–1173 K and $n = 1$. It is completely absent from the system with $n = 0.5$. At the same time, a decrease in the area of the endo-effect was observed; this fact is assigned to the process of desulphurization in the 1053–1173 K temperature range. Obviously, the lower weight losses obtained for the process of iron sulphate decomposition result from the chemical interactions, taking place in the 553–673 K temperature range.

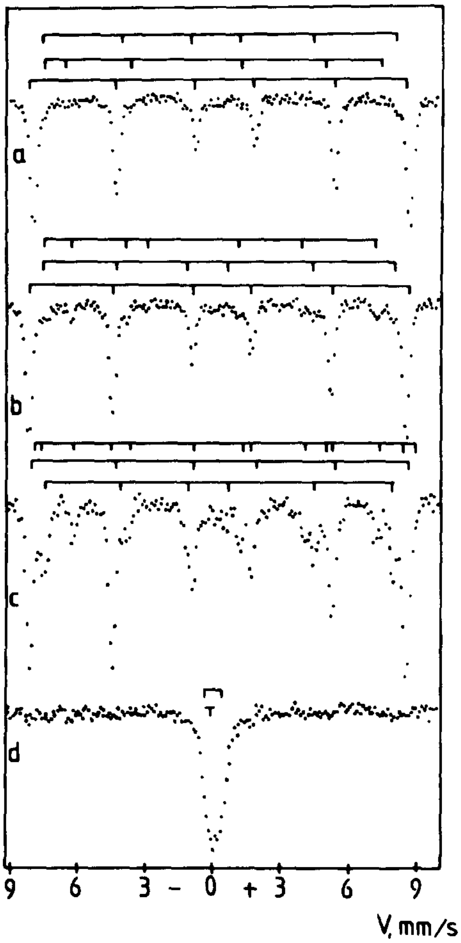

Fig. 6. Mössbauer spectra of the solid products of the thermal decomposition at $V = 5$ K $\min^{-1}$ in oxidizing gaseous medium and $T = 1273$ K of: a) the mixture with $n = 4$; b) the mixture with $n = 2$; c) the mixture with $n = 1$; d) the mixture with $n = 0.5$.

The X-ray analysis of the end product from decomposition of the mixture with $n = 0.5$ proved the existence of $BaSO_4$ and $BaFeO_3$. Obviously, the greater the quantity of BaO_2 in the system, the greater is the possibility of obtaining ferrites with a Ba:Fe ratio closer to 1. The Mössbauer spectrum of the end product from decomposition of mixture with $n = 0.5$ is presented in Fig. 6d. It shows a complex spectrum with overall isometric shift of almost 0.11 mm s^{-1}, which is formed by the superimposition of a single band and several doublets. These doublets have isometric shift close to zero and ΔE_Q up to 0.6 mm s^{-1}. This superimposition is characteristic of compounds with perovskite structure of the $BaFeO_3$ type with non-stoichiometric oxygen content and corresponding statistical distribution of the non-equivalent ferrite atoms in relation to the close O^{2-} environment. Similar spectra have been also reported by Gallagher et al. [9]. This small isometric shift could be interpreted as Fe^{4+} or as an iron atom with great electron density, namely a strongly expressed covalent bond. As a result of this, the Mössbauer spectrum is presented by isometric shift with a value close to that of iron. The high conductivity of this type of "oxide" gives ground for accepting the second explanation as more plausible. The Mössbauer spectra of the end products from decomposition of other mixtures are presented in Figs. 6a–6c. They confirm the existence of various magnetically ordered phases, with the largest quantity - that of α-Fe_2O_3. In the Mössbauer spectra (Figs. 6b and 6c), along with the sextet of α-Fe_2O_3, the $BaFe_2O_4$ sextet is also recorded, as well as the main and strongest bands of the spectrum of $BaFe_{12}O_{19}$. Its spectrum is very complex and is composed of five sub-spectra (five sextets), each of them allocated to the corresponding crystallographic iron position [10, 11]. In view of the complex structure of $BaFe_{12}O_{19}$ and its small quantities in the samples (Figs. 6a–6c), this compound is verified on basis of the existence of the strongest band 12k in its spectrum. Taking into account the same considerations, it is possible to explain the lack of $BaFe_{12}O_{19}$ in the data recorded from the X-ray phase analysis.

On basis of the investigations carried out on the thermochemical decomposition of the MhFS–BaO_2 system at various molar ratios in an oxidizing gaseous medium and dynamic heating regime, the following sets of interactions could be implied.

With excess iron sulphate the decomposition process proceeds according to the following stages:

553–613 K

$$BaO_2 = BaO + 1/2O_2 - Q \tag{1}$$

$$FeSO_4 \cdot H_2O + BaO_2 = BaSO_4 + BaFeO_3 + H_2O + 1/2O_2 + Q \tag{2}$$

$$FeSO_4 \cdot H_2O = FeSO_4 + H_2O - Q \tag{3}$$

$$2FeSO_4 \cdot H_2O + 1/2O_2 = 2FeOHSO_4 + H_2O - Q \tag{4}$$

$$2FeSO_4 \cdot H_2O + 1/2O_2 = Fe_2O(SO_4)_2 + 2H_2O - Q \tag{5}$$

613–659 K

$$FeOHSO_4 + 2BaO_2 = BaFeO_3 + BaSO_4 + 1/2H_2O + 3/4O_2 + Q \tag{6}$$

$$3/2BaFeO_3 + 1/2FeOHSO_4 = BaFe_2O_4 + 1/2BaSO_4 + 1/4H_2O + 3/8O_2 + Q \tag{7}$$

$$FeOHSO_4 + 3/2BaO = 1/2BaFe_2O_4 + BaSO_4 + 1/2H_2O + Q \tag{8}$$

773–793 K

$$2FeOHSO_4 = Fe_2O(SO_4)_2 + H_2O - Q \tag{9}$$

$$2FeSO_4 + 1/2O_2 = Fe_2O(SO_4)_2 + Q \tag{10}$$

883–1063 K

$$Fe_2O(SO_4)_2 + 2BaFeO_3 = 2BaFe_2O_4 + SO_2 + 3/2O_2 - Q \tag{11}$$

$$11/2Fe_2O(SO_4)_2 + BaFeO_3 = BaFe_{12}O_{19} + 11SO_2 + 23/4O_2 - Q \tag{12}$$

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_2 + O_2 - Q \tag{13}$$

$$2FeSO_4 = Fe_2O_3 + 2SO_2 + 1/2O_2 - Q \tag{14}$$

The suggested chemical mechanism for the thermal decomposition of mixtures with excess MhFS is in accordance with the recorded weight losses and data for the intermediate and end products, identified using different physico-chemical procedures. The phase content and quantity of the compounds in real-life test settings are defined by the temperature, partial pressures of the gas components and ratio between rates of the separate reactions.

At higher oxygen content ($n = 1$) the process proceeds in two principal temperature intervals:

533–543 K

$$FeSO_4 \cdot H_2O = FeSO_4 + H_2O - Q \tag{3}$$

$$FeSO_4 + 2BaO_2 = BaFeO_3 + BaSO_4 + 1/2O_2 + Q \tag{15}$$

1053–1173 K

$$FeSO_4 + BaFeO_3 = BaFe_2O_4 + SO_2 + 1/2O_2 - Q \tag{16}$$

$$11FeSO_4 + BaFeO_3 = BaFe_{12}O_{19} + 11SO_2 + 3O_2 - Q \tag{17}$$

$$2FeSO_4 = Fe_2O_3 + 2SO_2 + 1/2O_2 - Q \tag{14}$$

With a greater excess of BaO_2 ($n = 0.5$) the process proceeds in one stage:

613 K

$$FeSO_4 \cdot H_2O + 2BaO_2 = BaFeO_3 + BaSO_4 + H_2O + 1/2O_2 + Q \tag{18}$$

4. Conclusion

The studies carried out on the thermal decomposition of MhFS–BaO_2 mixtures prove the complexity of the interactions between the reagents. The determinative influence of the temperature and partial pressure of the gaseous components on the rate of the processes has been established, as well as the formation of the intermediates, such as $FeOHSO_4$ and $Fe_2O(SO_4)_2$. On the basis of the results provided by the Mössbauer spectroscopy, thermal and X-ray analysis, a process mechanism at different molar ratio between the system components has been suggested.

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