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COMPARATIVE DSC STUDY ON THERMAL DECOMPOSITION OF IRON SULPHATES

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The objects for the studies of this paper are iron sulfates where the iron has second or third valences and where coordination between iron, sulfur and oxygen is different. DSC technique is used to investigate thermal stability and enthalpy changes when iron compounds are treated in different gas medium. The main objective is to compare thermal stability and enthalpy of iron oxy-sulphate, often detected as an intermediate, with commonly known iron sulphates.

DSC curves of samples with equal mass under different gas medium, determining different partial pressure of oxygen in the gas phase, are the base for comparative study of the sample's thermal properties. Obtained different values of the enthalpy and mass losses and kinetic parameters demonstrate that the stability of oxy-sulphate strongly depended on the value of oxygen partial pressure in the gas phase.

The new evidences from the experimental study help to propose the mechanism of the decomposition and to compare some of the iron sulphates properties.

Keywords: *decomposition, DSC, gas medium, iron sulphates, thermal properties*

Introduction

Metastabillity of iron sulphates like ($FeOHSO_4$ and $Fe_2O(SO_4)_2$) and difficulties to isolate them as pure phases keep the scientific interest on their behaviour during thermal decomposition processes [1–4]. It was found that $FeOHSO_4$ and $Fe_2O(SO_4)_2$ could be obtained as a pure phase during thermal process treatment of $FeSO_4$-hydrate intermediates only if specific experimental conditions are set (process mechanism is sensitive to the heating rate, partial pressure of gas components like oxygen, water vapour, sulphur oxides, etc.) [1–5]. Identification of $FeOHSO_4$ [6] and especially of $Fe_2O(SO_4)_2$ [7] is also uneasy, because for number of methods the characteristics of intermediates are very close to the $Fe_2(SO_4)_3$. In previous publication [5] we have presented a data, related to the use of some spectroscopy methods for identification of $Fe_2O(SO_4)_2$. Up to now comparative DSC studies at the same conditions for different iron sulphates are not available. Different equipment and conditions used, gives explanation for the differences registered [1, 2].

The aim of this paper is to present the results obtained using the same experimental conditions and techniques on the way to be correct in our conclusions and comparisons. DSC curves of the thermal decomposition of $FeSO_4{\cdot}H_2O$, $FeSO_4$, $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ in argon, air and oxygen atmosphere are presented as a follow up study of our previous publications on ($FeSO_4{\cdot}H_2O$ and $FeSO_4$) [8] and ($Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$) [9].

Experimental

$FeSO_4$ is obtained by heating of $FeSO_4{\cdot}7H_2O$ in an inert argon atmosphere up to 743 K. $Fe_2(SO_4)_3$ is produced by heating of $Fe_2(SO_4)_3{\cdot}xH_2O$ ($x \leq 9$) in the same atmosphere, but at temperatures up to 773 K. $FeSO_4{\cdot}H_2O$ was produced by a preliminary drying of $FeSO_4{\cdot}7H_2O$ at 353 K in a vacuum of $0.6{\cdot}10^{-5}$ Pa. The dried product contained 55.93% SO_4^{2-}, 34.57% Fe^{2+} and 9.5% crystallization water. $Fe_2O(SO_4)_2$ is a product from thermal treatment of $FeSO_4{\cdot}H_2O$ at 813 K during 30 min in an oxygen flow rate. $Fe_2O(SO_4)_2$ origin is described in [5].

DSC is applied as an experimental method for characterization of physical and chemical transformations of the substances treated [10–13]. From obtained DSC curves C_p–T relationship is derived. Heat effect (ΔH_t) is calculated from DSC curves also on the base of heat flow (mJ s^{-1}) and temperature values during treatment, using Eq. (1).

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$$\Delta H = k\int_{t}^{t'} \Delta T \mathrm{d}t = kA \qquad (1)$$

where t is the experimental time (t at the start point and t' – end of the heat effect); ΔT is the temperature differences between sample studied and reference used; κ the equipment constant; A is the DSC peak area. Equipment constant is determined on the base of Zn and I standards used for calibration procedure. On the base of the k value heat effects are calculated using Eq. (2).

$$\Delta H_{\mathrm{t}} = kA \qquad (2)$$

In the case of overlapping of some intermediate transformations estimations are done on the base of the shape of thermal effects registered. It is the case of second and third stage transformation of $FeSO_4 \cdot H_2O$ in argon atmosphere and the initial stage for $FeSO_4 \cdot H_2O$ in oxygen media. The C_{p} – temperature relationship is calculated on the base of sapphire reference experiments and Eq. (3).

$$(C_{\mathrm{p}})_{\mathrm{t}} = \frac{(\Delta T_{\mathrm{s}} + \Delta T_{\mathrm{sa}} + \Delta T_{\mathrm{c}})K_{\mathrm{t}}}{ma} \qquad (3)$$

where $(C_{\mathrm{p}})_{\mathrm{t}}$ is the specific heat capacity at temperature T (mJ mg^{-1} K^{-1}); ΔT_{s} – absolute temperature sample difference, K; ΔT_{sa} – absolute sapphire difference, K; ΔT_{sa} – absolute temperature difference for empty cruicible, K; K_{t} – calibration constant at temperature T, mJ mg^{-1} K^{-1}, m – sample mass, mg; a – heating rate, min K^{-1}.

DSC Stanton Redcroft thermal analyzer in the temperature range 293–1400 K, heating rate 10 K min^{-1}, mass sample of 2 mg and Pt crucibles with inner diameter of 4.5 mm are applied. Flow rate of argon, dried air or oxygen is 50 mL min^{-1}.

Results and discussion

Sensitivity of the thermal decomposition process of $FeSO_4 \cdot H_2O$ and $FeSO_4$ to partial pressure of oxygen and water vapor keep is already mentioned by different researchers [2, 6]. This was the reason 3 gas environments with different oxygen content to be used. The results from DSC investigations are presented on Figs 1–8. Determined on the base of the DSC curves, temperature ranges, inflection points and ΔH_{t} values are given in Tables 1–3. Total mass losses are also determined on the base of independed measurements.

$FeSO_4 \cdot H_2O$ decomposition in different gas media

As it can be seen from the Fig. 1 DSC curves of $FeSO_4 \cdot H_2O$ is the most sensitive to the gas media in comparison to other iron sulphates. In the temperature 293–1400 K step by step the processes of dehydration, oxidation and finally thermal decomposition take place. In the argon atmosphere four endothermic effects are registered. The obtained data from previous studies have shown [8] that the endothermic peak at 551.8 K (Table 1) indicates the last water molecule releasing and this is the end of dehydration process. In the argon atmosphere the oxidation reactions are suppressed and the dehydration process has a higher rate. ΔH_{t} for dehydration in this case is 99.8 kJ mol^{-1}. The next step endothermic peak (T_{infl}=859.9 K, Table 1) is related to the thermal decomposition of $FeSO_4$ to $Fe_2O(SO_4)_2$ and Fe_2O_3 [8]. Possible explanation about is the generation of oxygen from the reactions and the existing small amount of oxygen in the carrier argon gas. The last intensive endothermic peak (T_{infl}=931.0 K, Table 1) is a result of thermal decomposition of both sulphates (the formed $Fe_2O(SO_4)_2$ and remaining $FeSO_4$) to Fe_2O_3 and SO_3 or SO_2 and O_2).

When air is used as a carrier gas the DSC curves of $FeSO_4 \cdot H_2O$ are characterized with 3 endothermic peaks – the first two, quite small and the last one, consuming the highest quantity of energy (Fig. 1, Table 2).

Heat capacity of the $FeSO_4 \cdot H_2O$ and $FeSO_4$ can not be determined clearly because the thermal stability of the substances is affected during treatment in different carrier gas (Figs 5 and 6). It is due to the complicated chemical mechanism and new solid phase's formation. For $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ where decomposition mechanism does not change the phase composition gas atmosphere does not affect heat capacity dependence.

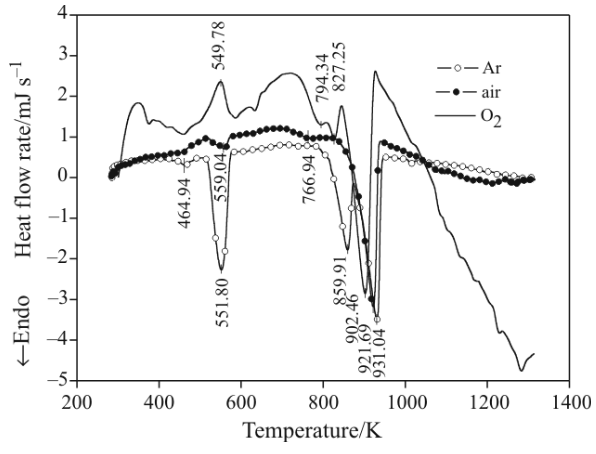

Fig. 1 Heat flow rate as a function of temperature for $FeSO_4 \cdot H_2O$ 10 K min^{-1}, different gas media

Table 1 Values, determined from DSC studies (Ar carrier gas), for some iron sulphates

Substance	Argon environment				
	T_{start}/K	T_{end}/K	T_{infl}/K	ΔH_{total}/kJ mol^{-1}	Total mass losses/%
			$FeSO_4$		
I – decomposition	763.2	872.2	842.5	177.6	
II – decomposition	810.8	944.2	913.2	331.1	48.2
			$FeSO_4{\cdot}H_2O$		
I – dehydration	438.2	492.4	464.9	3.7	
II – dehydration	492.4	578.7	551.8	96.1	
III – decomposition	778.3	878.1	859.9	88.8	
IV – decomposition	878.1	949.7	931.0	157.1	53.0
			$Fe_2(SO_4)_3$		
I – decomposition	755.4	944.1	921.0	439.7	58.4
			$Fe_2O(SO_4)_2$		
I – decomposition	766.6	953.9	933.7	347.1	47.3

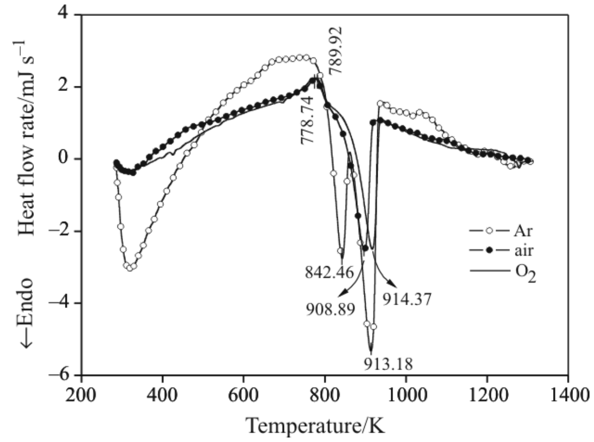

Fig. 2 Heat flow rate as a function of temperature for $FeSO_4$ 10 K min^{-1}, different gas media

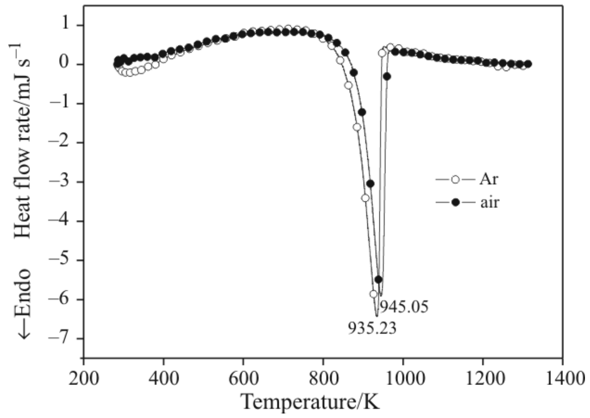

Fig. 3 Heat flow rate as a function of temperature for $Fe_2O(SO_4)_2$ 10 K min^{-1} in argon and air media

The first endothermic peak corresponds to the releasing of the last crystal water. The peak area is smaller, because of the partial oxidation reaction to the intermediate $FeOHSO_4$. This is the reason that in the DSC curve of $FeSO_4{\cdot}H_2O$ in air medium, is registered a limited peak area at 559 K (Fig. 1, Table 2). The presence of water vapor (dehydration of crystal water from $FeSO_4{\cdot}H_2O$) and oxygen from the carrier gas support the formation of $FeOHSO_4$. We should point out that at that temperature range formation of $Fe_2O(SO_4)_2$ and $Fe_2(SO_4)_3$ is also possible in view of thermodynamics [1, 4]. The second endothermic peak (T_{infl}=766.9 K, Table 2) is a result of two overlapping reactions – decomposition of $FeOHSO_4$ to $Fe_2O(SO_4)_2$ and water vapour (endothermic effect) and oxidation of $FeSO_4$ to $Fe_2O(SO_4)_2$ (exothermic reaction) [1, 8]. The limited area of the registered peak we explain with the compensation of both endo- and exothermic effects. It should be pointed out that $FeOHSO_4$ has slightly lower thermal stability and during its decomposition water vapor is released in the same temperature interval [1, 3, 6, 8]. Direct oxidation of $FeSO_4$ to $Fe_2O(SO_4)_2$ was proved [1, 3, 5] and it should be taken into account that the presence of oxygen in the gas phase accelerate the rate of oxidation. The shape and area of the last endothermic peak (T_{infl}=921.7 K, Table 2) describe the thermal decomposition of $FeSO_4$ and $Fe_2O(SO_4)_2$ to Fe_2O_3 and SO_2+O_2).

DSC curve of the $FeSO_4{\cdot}H_2O$ in oxygen environment is quite different. Just the opposite to the other carrier gases, the first peak at 549.8 K (Fig. 1, Table 3) is exothermic with relatively large area. Such an effect could be explained by the proceeding of direct oxidation of $FeSO_4{\cdot}H_2O$ to $FeOHSO_4$ and $Fe_2O(SO_4)_2$. Both reactions are exothermic and the released water confirmed that. The next two, partially overlapping peaks, are result of decomposition of

Table 2 Values, determined from DSC studies (air carrier gas), for some iron sulphates

Substance	Air environment				
	T_{start}/K	T_{end}/K	T_{infl}/K	ΔH_{total}/kJ mol^{-1}	Total mass losses/%
$FeSO_4$					
I – decomposition	332.1	825.4	788.3	297.1	
II – decomposition	825.4	933.4	908.4	159.9	49.5
$FeSO_4{\cdot}H_2O$					
I – dehydration	517.7	576.9	559.0	8.9	
II – decomposition	707.3	813.8	766.9	6.5	
III – decomposition	813.8	939.6	921.7	159.8	52.5
$Fe_2(SO_4)_3$					
I – decomposition	746.6	962.0	932.4	407.3	59.6
$Fe_2O(SO_4)_2$					
I – decomposition	791.2	968.0	945.1	293.2	48.8

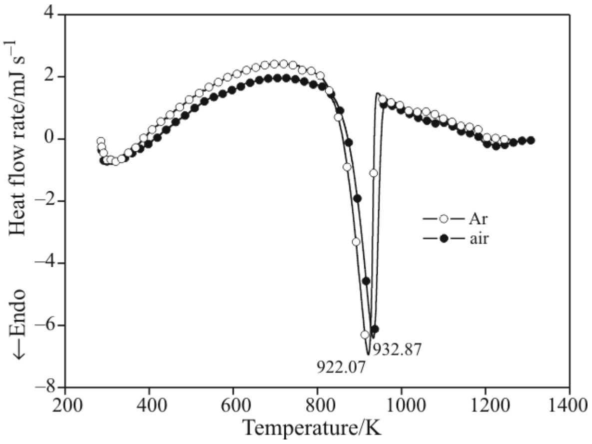

Fig. 4 Heat flow rate as a function of temperature for $Fe_2(SO_4)_3$ 10 K min^{-1} in argon and air media

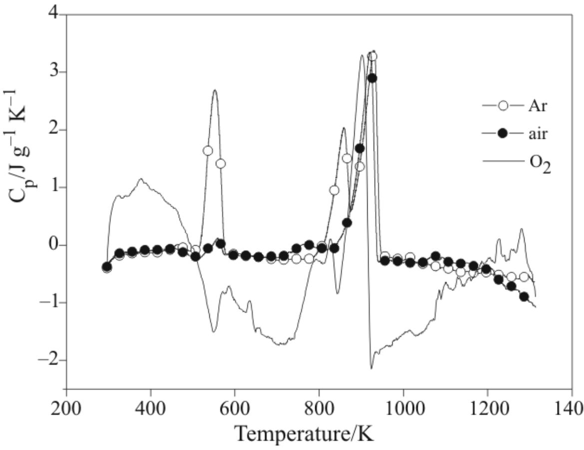

Fig. 5 Heat capacity of $FeSO_4{\cdot}H_2O$ in argon, air and oxygen

$FeOHSO_4$ to $Fe_2O(SO_4)_2$ and water vapor (T_{infl}=794.3 K, Table 3) and the last decomposition of $Fe_2O(SO_4)_2$ (T_{infl}=902.5 K, Table 3) to Fe_2O_3 and SO_2+O_2. We have to state that this the first time to have a possibility to obtain separate peaks for those two reactions.

$FeSO_4$ decomposition in argon atmosphere

On the DSC curve two endothermic peaks are registered. The first one (T_{infl}=842.5 K, Fig. 2, Table 1) is a result of $Fe_2O(SO_4)_2$ and Fe_2O_3 formation as it was for $FeSO_4{\cdot}H_2O$. In this temperature range is possible also a reaction to the $Fe_2(SO_4)_3$, but the studies in [8], have proved that the mass losses correspond to the first reaction. The second endothermic peak is related to the complete desulphurization reactions producing Fe_2O_3 and SO_2 (and O_2).

$FeSO_4$ in air and oxygen atmosphere

Increasing content of oxygen does not affect chemical mechanism, but it has some influence on the rate of oxidation to $Fe_2O(SO_4)_2$. As it can be seen from Fig. 2 and Tables 2 and 3 that the higher partial pressure of oxygen that the registered peaks are in the same temperature ranges, but the peak's area for the oxidation step is increasing. ΔH_t is 365.9 kJ mol^{-1} in oxygen atmosphere, when in the argon atmosphere it is only 177.6 kJ mol^{-1}. Gas environment do not affect the second stage of the process related to the transformation of $Fe_2O(SO_4)_2$ to Fe_2O_3 and SO_2+O_2.

$Fe_2(SO_4)_3$ in argon and air environment

Data presented on Fig. 3 and Table 1 determine the decomposition process as a one-stage transformation, related to the desulfurization of the $Fe_2(SO_4)_3$ to Fe_2O_3 and SO_2 and O_2. ΔH_t values are quite close, but

Table 3 Values, determined from DSC studies (oxygen carrier gas), for some iron sulphates

Substance	Oxygen environment				
	T_{start}/K	T_{end}/K	T_{infl}/K	ΔH_{total}/kJ mol^{-1}	Total mass losses/%
			$FeSO_4$		
I – oxidation	321.6	810.2	771.9	365.9	
II – decomposition	810.2	938.9	916.4	306.9	51.3
			$FeSO_4{\cdot}H_2O$		
I – dehydration	461.3	586.3	549.8	48.3	
II – decomposition	720.2	803.3	794.3	24.3	
III – decomposition	807.6	844.7	827.3	60.4	
IV – decomposition	844.7	927.4	902.5	262.6	62.0

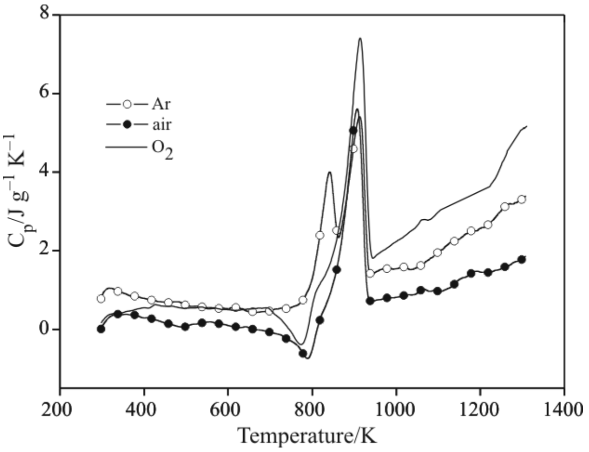

Fig. 6 Heat capacity of $FeSO_4$ in argon, air and oxygen

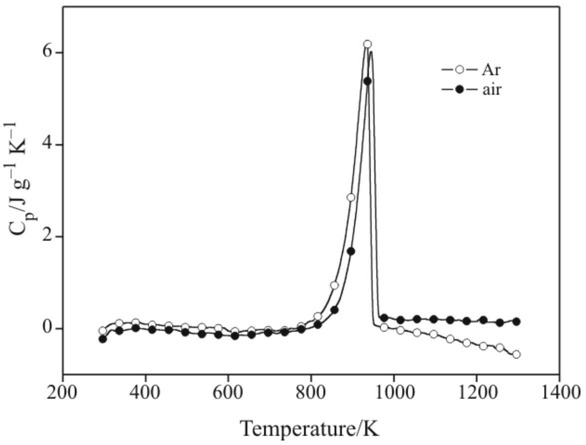

Fig. 7 Heat capacity on $Fe_2O(SO_4)_2$ in argon and air

there is some difference in the T_{inf} – from 921 to 932.4 K. This is indication for some changes in the rate of decomposition. It could be simply due to the difference in the heating conductivity of the carrier gas. Total mass losses also confirm that the final products are Fe_2O_3 and SO_2 and O_2. Such a conclusion was made also on the base of the results of previous studies [9]. As the final solid product is Fe_2O_3 the heat capacity is the same for the carrier gases used (Fig. 7, Tables 1 and 2).

$Fe_2O(SO_4)_2$ decomposition in the argon and air environment

Firstly it should be stated that in the case of $Fe_2O(SO_4)_2$, the balance of oxygen gives the possibility for decomposition to Fe_2O_3 when argon is used as a carrier gas. As it could be expected the one-stage decomposition process, as it is for $Fe_2(SO_4)_3$, is registered. By the way the DSC curves shown on Fig. 4 and data obtained given in Tables 1 and 2 are reported for the first time in the known literature. T_{infl} is 933.7 K for the argon environment and 945.1 K for the air environment. ΔH_t has a little bit lower values in the air environment. It could be due to two reasons – higher oxygen partial pressure in the air environment or different thermal conductivity of the carrier gas. Heat capacity is the same in the both gas environment phases and it is indirect confirmation that the same stable solid phase is obtained as a result of the thermal decomposition (Fig. 8, Tables 1 and 2).

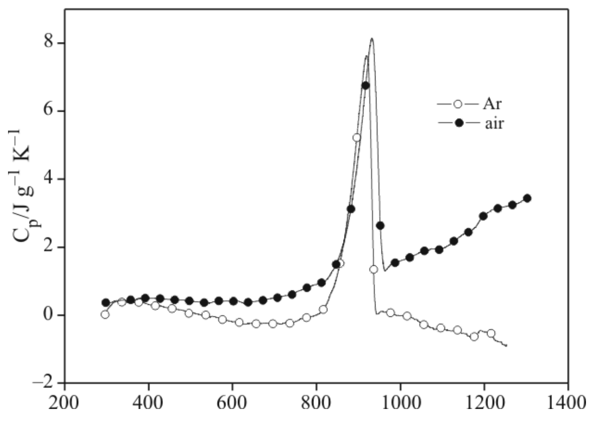

Fig. 8 Heat capacity on $Fe_2(SO_4)_3$ in argon and air

Conclusions

DSC studies made and new data obtained for the iron sulphates in different gas atmosphere in general are in a good agreement with results already published in our previous papers [1, 4, 5, 8, 9]. The same time we may consider them as new evidences for the processes of thermal decomposition of the iron sulphates. It is demonstrated that the partial pressure of the gas components in the gas phase are of great importance for thermal decomposition of the iron sulphates where the iron is in the second valence. Formation of $FeOHSO_4$ and $Fe_2O(SO_4)_2$ as intermediates are the most sensitive to water vapor and oxygen content and it is confirmed by the shape of DSC curves and heat capacity dependences. Gas phase content is not of such an importance for thermal decomposition of $Fe_2(SO_4)_3$ and $Fe_2O(SO_4)_2$ where decomposition mechanism is due only to formation of Fe_2O_3 as a final solid product.

References

1 Y. Pelovski, V. Petkova and S. Nikolov, Thermochim. Acta, 274 (1996) 273.

2 R. Zboril, M. Mashlan and D. Petridis, Chem. Mater., 14 (2002) 969.

3 R. Zboril, M. Mashlan, D. Petridis, D. Krausova and P. Pikal, Hyperfine Interactions, 139 (2002) 437.

4 Y. Pelovski and V. Petkova, J. Thermal Anal., 49 (1997) 1227.

5 V. Petkova and Y. Pelovski, J. Therm. Anal. Cal., 64 (2001) 1025.

6 G. Ventruti, F. Scordari, E. Schingaro, A. F. Gualtieri and C. Meneghini, Am. Mineral., 90 (2005) 679.

7 V. Petkova and Y. Pelovski, J. Therm. Anal. Cal., 64 (2001) 1037.

8 V. Petkova, Y. Pelovski, Y. Kulvachev, O. Petrov, D. Paneva and I. Mitov, Influence of Gas Phase on the Thermochemical Decomposition of Iron Second Valence, J. Univ. Chem. Technol. Met., Sofia, (in print).

9 V. Petkova and Y. Pelovski, J. Envir. Prot. Ecology, (in print).

10 F. Fraga, V. H. Soto, J. Blanco-Méndez, A. Luzardo-Alvarez, E. Rodríguez-Núñez, J. M. Martínez-Ageitos and M. Pérez, J. Therm. Anal. Cal., 87 (2007) 233.

11 F. Román, S. Montserrat and J. M. Hutchinson, J. Therm. Anal. Cal., 87 (2007) 113.

12 Ž. Mesíková, P. Šulcová and M. Trojan, J. Therm. Anal. Cal., 84 (2006) 733.

13 Ž. Mesíková, P. Šulcová and M. Trojan, J. Therm. Anal. Cal., 83 (2006) 561.

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