

MÖSSBAUER STUDIES OF THE PHASE FORMATION IN THE Fe-S SYSTEM

B. Korzun¹, V. Sobol¹, M. Myndyk², V. Šepelák³, K. D. Becker²

¹*Belarusian State Pedagogical University, Minsk, Belarus, vrsobol@mail.ru*

²*Braunschweig University of Technology, Braunschweig, Germany*

³*Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany*

Annotation. The phase formation in the Fe-S system was investigated by differential thermal analysis and Mössbauer spectroscopy. It was found that the formation of FeS compound takes place after melting of sulphur in the temperature range from 490 to 590 K. Mössbauer parameters of the quenched samples allowed attributing the thermal peak at temperatures 590-620 K to formation of FeS₂, which at the subsequent heating decomposes on peritectics at 1015 K. A full description of the alloys by DTA, XRPD, and Mössbauer studies allowed to make recommendations for the technology of preparation of multinary compounds with crystal structures of chalcopyrite CuFeS₂, kesterite Cu₂(Zn, Fe)SnS₄, stannite Cu₂FeSnS₄, and compounds existing in the Cu-Fe-S system.

INTRODUCTION

Multinary Fe-containing semiconducting compounds with crystal structures of chalcopyrite CuFeS₂, kesterite Cu₂(Zn, Fe)SnS₄, and stannite Cu₂FeSnS₄ are at the focus of current research as absorbing materials in solar cells [1]. To obtain these materials with optimal physical characteristics it is necessary to know the processes of phase formation during preparation of such materials from chemical elements, especially for the binary system Fe-S where compounds Fe_{1-x}S (pyrrhotite) and pyrite FeS₂ (in structure of pyrite and marcasite) exist. Although T-x phase diagram of the Fe-S has been investigated and constructed there are a lot of contradictory results especially for the central part of this system at low temperatures [2]. The goal of this paper is to study the phase formation in the Fe-S system and to achieve this goal, the mixtures of the elements were heated in DTA apparatus, quenched following the corresponding thermal peaks, and then investigated using XRPD and Mössbauer studies.

EXPERIMENTAL

The mixtures of Fe and S with the atomic ratios Fe:S = 1:1; 1:2, and 2:3 were investigated. The X-ray studies were carried out using monochromatic Cu K_α-radiation (1,5406 Å, step size 0,01° or 0,04°, counting time 10 s). The DTA measurements were performed using special carriers within a high-temperature steel clamp. The temperatures of the structural phase transitions were determined using Pt/90%Pt-10%Rh thermocouples with the heating rates being 2-3 K/min (accuracy of ±2 K). Reproducible results were obtained by placing powder samples of 1 g in evacuated (1,3·10⁻² Pa) quartz capsules using Al₂O₃ as a reference material. Room-temperature ⁵⁷Fe Mössbauer spectra were taken in transmission geometry using a ⁵⁷Co/Rh γ-ray source. The velocity scale was calibrated relative to ⁵⁷Fe in Rh.

RESULTS AND DISCUSSION

It was found that up to the melting point of sulphur (Fig. 1 and Fig. 2, peak A) there is no essential formation of iron sulphides. The thermal peak B₁, associated with the formation of FeS is divided into two subpeaks with maximums at 522 and 576 K. Such shape is formed because simultaneously with the formation of iron sulphides (exothermic peak) crystallographic transitions (endothermic peaks) occur. Mössbauer parameters of the quenched samples coincided with the parameters of FeS and FeS₂ [3, 4] and it allowed attributing the thermal peak at temperatures 590–620 K to formation of FeS₂, which at the subsequent heating decomposes on peritectics at 1015 K.

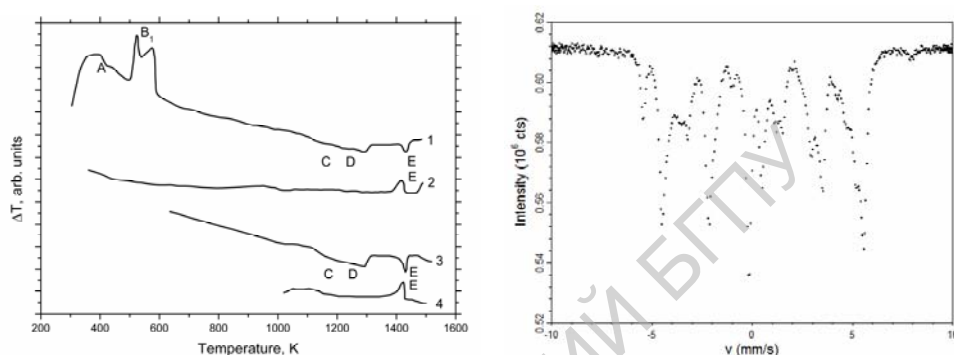


Figure 1. – Thermogram of the mixture of chemical elements Fe:S = 1:1 (atomic ratio) /left picture/ and Mössbauer spectrum of this mixture after heating up to 800 K and quenching /right picture/ (1 – the first heating of the mixture, 2 – the cooling of the chemical elements preheated in the process 1, 3 – the repeated heating of the mixture, 4 – the cooling of the chemical elements preheated in the process 3)

A complex endothermic peak at 1200 - 1261 K appears at further heating. This peak is the superposition of thermal peaks caused by the peritectoid transformation $\gamma\text{-Fe} + \text{FeS} \leftrightarrow \alpha\text{-Fe}$ (peak C) and eutectics reaction $\gamma\text{-Fe} + \text{FeS}$ (peak D). A detailed description of all thermal peaks is presented in Table 1.

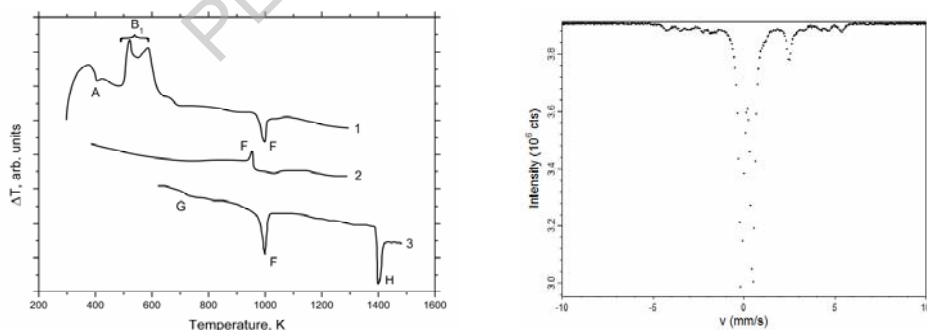


Figure 2. – Thermogram of the mixture of chemical elements Fe:S = 1:2 (atomic ratio) /left picture/ and Mössbauer spectrum of this mixture after heating up to 800 K and quenching /right picture/ (1 – the first heating of the mixture, 2 – the cooling of the chemical elements preheated in the process 1, 3 – the repeated heating of the mixture)

A full description of the alloys by DTA, XRPD, and Mössbauer studies allowed to make recommendations for the technology of preparation of multinary compounds with crystal structures of chalcopyrite CuFeS_2 , kesterite $\text{Cu}_2(\text{Zn, Fe})\text{SnS}_4$, stannite $\text{Cu}_2\text{FeSnS}_4$, and compounds existing in the Cu-Fe-S system.

Table

Nature of the thermal peaks at the interaction in the Fe-S system

Thermal peak	Temperature, K	Nature of thermal peak
A	388,2	Melting of sulphur
B ₁	490-590	Formation of FeS
B ₂	590-620	Formation of FeS ₂
C	1200	Peritectoid transformation $\gamma\text{-Fe} + \text{FeS} \leftrightarrow \alpha\text{-Fe}$
D	1261	Eutectics reaction $\gamma\text{-Fe} + \text{FeS}$
E	1461	Melting/ Crystallization of FeS
F	1016	Peritectics decomposition/ Formation of FeS ₂
G	700	Crystallographic transformation of FeS ₂ from the structure of marcasite into the structure of pyrite
H	1380	Monotectic reaction in the interval of compositions FeS-S

CONCLUSIONS

The alloys of the Fe-S system with the atomic ratios Fe:S = 1:1; 1:2, and 2:3 were investigated. It was found that the formation of FeS compound takes place after melting of sulphur in the temperature range from 490 to 590 K. The thermal peak is divided into two subpeaks with maximums at 522 and 576 K. Such shape is formed because simultaneously with the formation of iron sulphides (exothermic peak) crystallographic transitions (endothermic peaks) occur. Mössbauer parameters of the quenched samples allowed attributing the thermal peak at temperatures 590–620 K to formation of FeS₂, which at the subsequent heating decomposes on peritectics at 1015 K. A full description of the alloys by DTA, XRPD, and Mössbauer studies allowed to make recommendations for the technology of preparation of multinary compounds with crystal structures of chalcopyrite CuFeS_2 , kesterite $\text{Cu}_2(\text{Zn, Fe})\text{SnS}_4$, stannite $\text{Cu}_2\text{FeSnS}_4$, and compounds existing in the Cu-Fe-S system.

Acknowledgement. B. Korzun and V. Sobol would like to thank the Belarusian Republican Foundation for Fundamental Research for financial support of the studies under project F15MLD-025.

REFERENCES

1. Siebentritt, S. Kesterites – a challenging material for solar cells/ S.Siebentritt, S.Schorr // Progress in Photovoltaics. – 2012. – 20, No. 5. – 512–519.
2. Kissin, S.A. Phase relations involving pyrrhotite below 350 degrees C/ S.A. Kissin, S.D. Scott// Economic Geology. – 1982. – 77, No. 7. – 1739-1754.
3. Fultz, B. Mössbauer Spectrometry/ B. Fultz// in Characterization of Materials, E. Kaufmann, Editor. - New York – John Wiley, 2011. – 23p.
4. McCammon, C. Mössbauer Spectroscopy of Minerals/ C. McCammon// in Mineral Physics and Crystallography: A Handbook of Physical Constants (AGU Reference Shelf 2); T.J. Ahrens, Editor. – 1995. – 332–347.