Combined DTA and Mössbauer Studies of the Fe-S System

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Abstract

The mixtures of Fe and S 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 FeS_2, which at the subsequent heating decomposes on peritectics at 1015 K.

Introduction and Motivation

What was the goal of this research project?

Multinary semiconducting compounds with crystal structures of chalcopyrite $CuFeS_2$, kesterite $Cu_2(Zn, Fe)SnS_4$, and stannite Cu_2FeSnS_4 are at the focus of current research as absorbing materials in solar cells. 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 FeS_2 (in structure of pyrite and marcasite) exist. The goal of this paper is to study the phase formation in the Fe-S system by means of combined DTA and Mössbauer studies.

Were there prior studies of the Fe – S system?

The T-x phase diagram of the Fe-S has been investigated and constructed. Nevertheless, there are a lot of contradictory results especially for the central part of this system at low temperatures [1] (Fig. 1).

Methods

Preparation

•The mixtures of Fe and S chemical elements with the atomic ratios Fe:S = 1:1, 1:2, and 2:3 were heated and quenched

Investigation

•X-ray powder diffraction, XRPD (K_α-radiation)

•Differential Thermal Analysis, DTA

•Mössbauer Spectroscopy

Results

•It was found that up to the melting point of sulphur there is no essential formation of iron sulphides. The formation of the 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 for the quenched samples allowed attributing the thermal peak at temperatures 590-620 K to formation of FeS_2 [2, 3], which at the subsequent heating decomposes on peritectics at 1015 K.

• A monotectic reaction in the range of composition FeS-S was confirmed at temperature 1380 K.

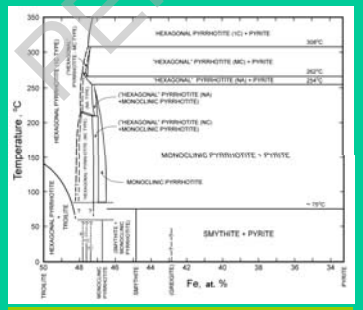

Fig. 1. A central part of T-x phase diagram of the Fe-S system at low temperatures [1]

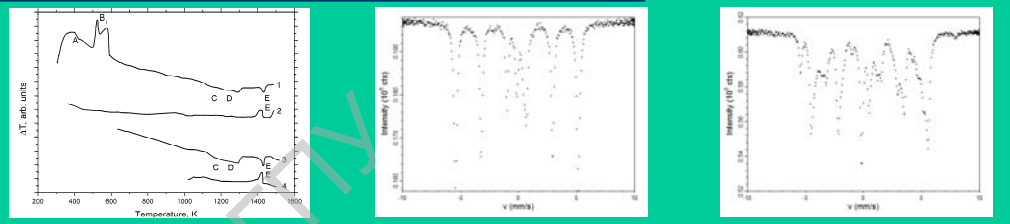

Fig. 2. Thermogram of the mixture of chemical elements Fe:S = 1:1 (atomic ratio) /left image/ and Mössbauer spectra of this mixture after heating up to 545 K and quenching /central image/ and after heating to 800 K and quenching /right image/

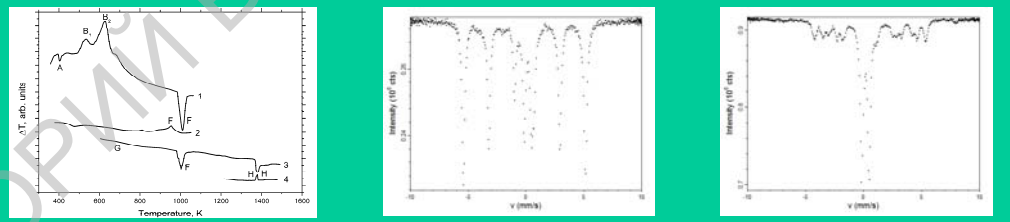

Fig. 3. Thermogram of the mixture of chemical elements Fe:S = 2:3 (atomic ratio) /left image/ and Mössbauer spectra of this mixture after heating up to 553 K and quenching /central image/ and after heating to 800 K and quenching /right image/

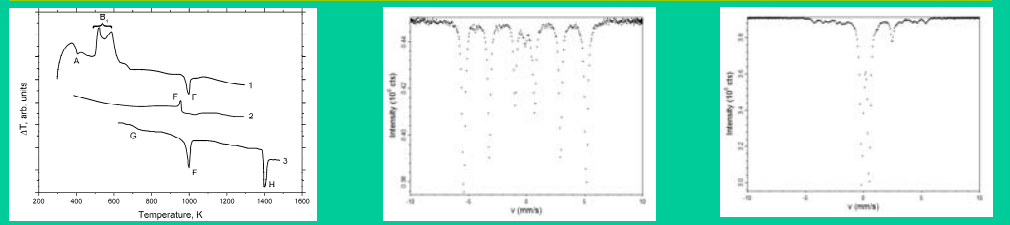

Fig. 4. Thermogram of the mixture of chemical elements Fe:S = 1:2 (atomic ratio) /left image/ and Mössbauer spectra of this mixture after heating up to 565 K and quenching /central image/ and after heating to 800 K and quenching /right image/

Conclusions

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 $Cu_2(Zn, Fe)SnS_4$, stannite Cu_2FeSnS_4, and compounds existing in the Cu-Fe-S system.

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