Mössbauer Studies of the $CuFeS_{2-\delta}$ - $CuInS_2$ System

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Abstract

The interaction in the $CuFeS_{2-\delta}$ - $CuInS_2$ system by means of Mössbauer studies and X-ray powder diffraction (XRPD) was studied using two series of alloys for $\delta = 0$ and $\delta = 0.10$ prepared from ternary compounds $CuFeS_{2-\delta}$ and $CuInS_2$ by a three stage solid state synthesis. XRPD revealed the absence of complete solubility in the $CuFeS_{2-\delta}$ - $CuInS_2$ and showed that the limit of solubility for $CuInS_2$-based alloys is 0.05 molar part and exceeds the limit of solubility for $CuFeS_{2-\delta}$ -based alloys (0.03 molar part). Mössbauer spectra of the $CuFeS_{2-\delta}$-$CuInS_2$ alloys in the two-field range for both $\delta = 0$ and $\delta = 0.10$ can be fitted by two components, a sextet and a doublet, indicating two different positions of iron atoms in the crystal lattice.

Introduction

Multinary semiconducting compounds with the crystal structures of chalcopyrite $CuFeS_2$ are at the center of current research as absorbing materials in solar cells. To obtain these materials with optimal physical characteristics it is necessary to know the phase equilibriums in these systems. The goal of this paper is to study the interaction in the $CuFeS_{2-\delta}$ - $CuInS_2$ system by means of Mössbauer studies and X-ray powder diffraction (XRPD).

Preparation of samples

The initial elements for the preparation of $CuInS_2$ and $CuFeS_{2-\delta}$ ternary compounds were 99.9998% copper, 99.9997% indium, 99.999% iron, and 99.9999% sulfur. Synthesis of the initial ternary compounds $CuInS_2$ and $CuFeS_{2-\delta}$ (with $\delta = 0$ and 0.10) was performed in quartz ampoules by melting chemical elements. Then two series of alloys for $\delta = 0$ and $\delta = 0.10$ with molar part of $CuInS_2$ (x) equal to 0.01, 0.03, 0.05, 0.125, 0.25, 0.375, 0.50, 0.625, 0.75, 0.875, 0.95, 0.97, and 0.99 were prepared from ternary compounds $CuFeS_{2-\delta}$ and $CuInS_2$ by a three stage solid state synthesis at 1073 K.

Methods

<u>X-ray studies</u>

- **were carried out using monochromatic Cu K_α-radiation (1.5406 Å, step size 0.01° or 0.04°, counting time 10 s).**

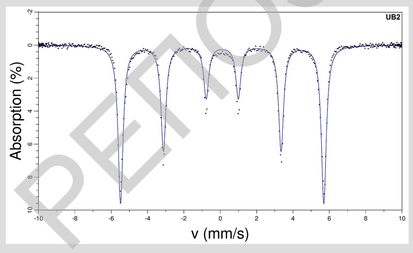
<u>Room-temperature ^{57}Fe Mössbauer spectra</u>

- **were taken in transmission geometry using a ^{57}Co/Rh γ–ray source. The velocity scale was calibrated relative to ^{57}Fe in Rh.**

Results

<u>XRPD</u>: X-ray powder diffraction revealed the absence of complete solubility in the $CuFeS_{2-\delta}$ - $CuInS_2$ system. Both the $CuInS_2$-based phase and the $CuFeS_{2-\delta}$-based phase crystallize in the tetragonal crystal structure. The limit of solubility for $CuInS_2$-based alloys is 0.05 molar part and exceeds the limit of solubility for $CuFeS_{2-\delta}$ -based alloys (0.03 molar part).

<u>Mössbauer studies</u>: The investigated samples revealed two different types of the Mössbauer spectra for the $CuFeS_{2-\delta}$-based alloys (sextet, IS = 0.114 mm/s, QS = -0.008 mm/s, H = 34.95 T, w = 0.195 mm/s) and for the $CuInS_2$-based alloys (doublet, IS = 0.124 mm/s, QS = (0.20 – 0.40 mm/s), w = 0.190 mm/s).



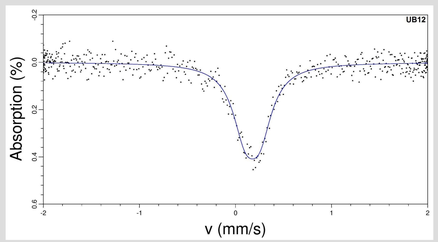
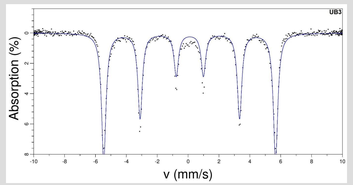


Figure 1. Mössbauer spectra of alloys with molar part of $CuInS_2$ x = 0.03 (UB2) and x = 0.97 (UB12) for $\delta = 0$.

Spectra and their fitting

Both Mössbauer spectra of the $CuFeS_{2-\delta}$-$CuInS_2$ alloys with $\delta = 0.10$ and $\delta = 0$ can be fitted by two components, a sextet and a doublet, indicating two different positions of iron atoms in the crystal lattice. The magnetic component (sextet) is due to the position of iron atoms in the tetragonal crystal structure of chalcopyrite $CuFeS_2$. The second component reflects the fact that there is no complete solubility in the $CuFeS_{2-\delta}$-$CuInS_2$ system and is due to the position of iron dopant in the crystal structure of the $CuInS_2$-based alloys.



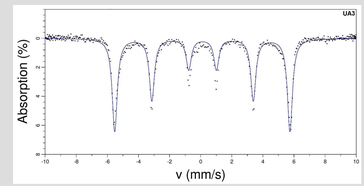
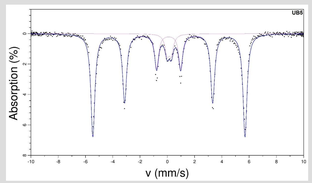


Figure 2. Mössbauer spectra of alloys with molar part of $CuInS_2$ x = 0.05 for $\delta = 0$ (UB3) and for $\delta = 0.10$ (UA3).



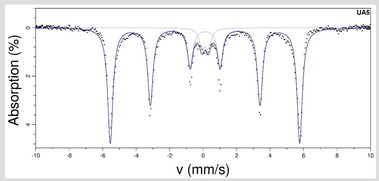
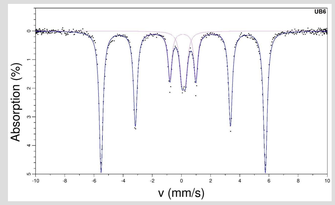


Figure 3. Mössbauer spectra of alloys with molar part of $CuInS_2$ x = 0.25 for $\delta = 0$ (UB5) and for $\delta = 0.10$ (UA5).



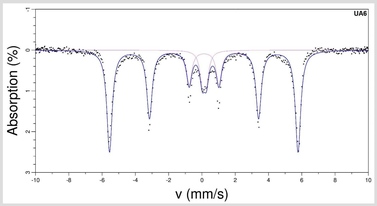


Figure 4. Mössbauer spectra of alloys with molar part of $CuInS_2$ x = 0.375 for $\delta = 0$ (UB6) and for $\delta = 0.10$ (UA6).

Conclusions

The influence of the variation of chemical composition of chalcopyrite $CuFeS_{2-\delta}$ with δ changing from 0 to 0.10 on the limits of solubility in the $CuFeS_{2-\delta}$ - $CuInS_2$ system was determined. The population of the second position of iron atoms approximated by the doublet for $CuFeS_{2-\delta}$-$CuInS_2$ alloys with $\delta = 0.10$ as compared with alloys with $\delta = 0$ indicates that the solubility region in the $CuFeS_{2-\delta}$ - $CuInS_2$ system is extended when using $CuFeS_{2-\delta}$ with $\delta = 0.10$ as the initial compound to prepare alloys.

Acknowledgments

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