UDC:546.56.86.22.15

POWDER X-RAY DIFFRACTION STUDY OF THE Cu_3SbS_3-CuI SYSTEM

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Received 03.08.2022
Accepted 28.11.2022

Abstract: *The nature of phase equilibria in the Cu_3SbS_3-CuI binary system over the entire concentration range were studied by means of the powder X-ray diffraction analysis (PXRD) for the first time at room temperature. It was found that the sample containing 66.7 mol.% CuI composed of a single phase and has a powder diffraction pattern completely different from the constituent phases of the system under study. The crystal lattice type and parameters, that were determined on the basis of the X-ray diffraction pattern of this sample using the TOPAS 4.2 and EVA computer programs are fully consistent with the literature data of the $Cu_5SbS_3I_2$ four-component compound. The copper (I) iodide rich samples of the system consist of a two-phase mixture of $Cu_5SbS_3I_2$ and CuI phases. However, the system is unstable in the $Cu_5SbS_3I_2$-Cu_3SbS_3 composition range. In this concentration interval, the system is characterized by complex physico-chemical interaction of the initial components.*
Keywords: *Cu_3SbS_3-CuI system, phase equilibria, lattice parameters, PXRD*
DOI: 10.32737/2221-8688-2023-1-57-63

Introduction

Chalcogenides, halides and chalcogen-halides of copper are widely studied due their interesting functional properties, in particular, their high ionic conductivity compared to Cu^+ cations [1-3]. Recent studies show that many natural chalcogenide minerals of copper such as chalcostibite ($CuSbS_2$), skinnerite (Cu_3SbS_3), famatinite (Cu_3SbS_4), tetrahedrite ($Cu_{12+x}Sb_{4+y}S_{13}$, $0 \le x \le 1.92$ and $0.02 \le y \le 0.27$) are a relatively new class of materials that can be utilized in thin-film solar cells, photoelectrochemical hydrogen production, etc. [4-7]. Among these copper antimony sulphide (CAS) materials, Cu_3SbS_3 is a semiconductor with a direct band gap value ranging between 1.46 - 1.84 eV and has high absorption coefficients making it a strong candidate as absorber and high performance thermoelectric candidate [8-10].

One of the approaches to search for new phases based on known compounds is the study of phase equilibria in relevant systems [11-13]. Because, the information accumulated in phase diagrams of the corresponding systems is always helpful in materials science for the development of advanced materials. In the context of the foregoing, here we report a study of phase equilibria of the Cu_3SbS_3-CuI system by PXRD method.

The presented work is a continuation of our research [14-18] in the field of metal chalcogenides and chalco-halides and is dedicated to the study of phase equilibria in the Cu_3SbS_3-CuI system.

Initial compounds of the system are well studied.

There are 3 modifications of the copper (I) iodide [19,20]. It was determined that the low-temperature γ-modification of CuI crystallizes in a face-centered cubic lattice and its transition to the β-phase occurs at 603K. The β-CuI phase crystallizes in a trigonal lattice, exists in a small temperature range (~10K) and transforms into the α phase at 613K [19]. The α-CuI phase also crystallizes in a cubic lattice [20].

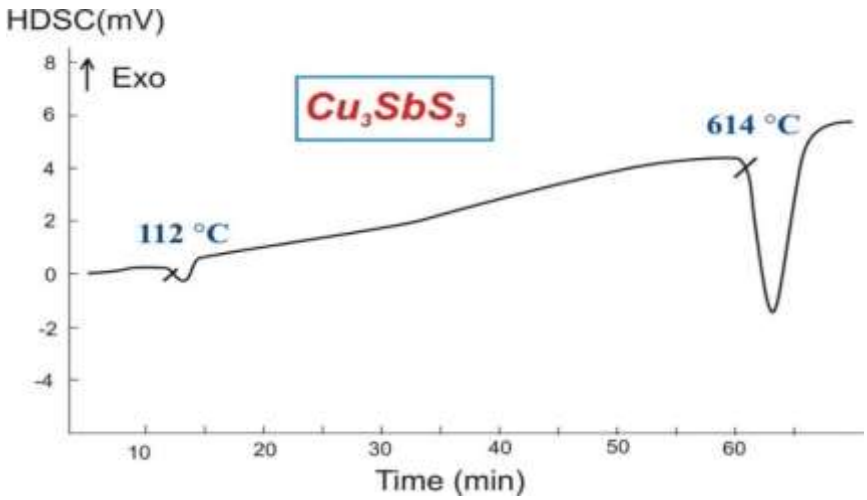
The Cu_3SbS_3 ternary compound, known as skinnerite mineral, melts congruently at 885K and exists in several modifications [21,22]. High-temperature α modification is stable at temperatures above 394K and has an orthorhombic crystal lattice. The intermediate β-Cu_3SbS_3 phase, which is stable in the temperature range of 264-395 K, crystallizes in a monoclinic structure. The low-temperature γ-modification of the Cu_3SbS_3 compound exists below 264K and has an orthorhombic crystal lattice.

Experimental part

Elemental copper (Cu-00029; 99.9999%), antimony (Sb-00002; 99.999%) and sulphur (S-00001; 99.999%) of high purity from Evochem Advanced Materials and CuI (7681-65-4, 99.999%) binary compound from the Alfa Aesar German brand were used for synthesis.

The Cu_3SbS_3 compound was synthesized by fusion of stoichiometric amounts of the corresponding simple substances in an evacuated (~10^{-2} Pa) and sealed silica ampoule of the 15 x1,5 cm size in a two-zone inclined furnace. The temperature of the hot zone of the furnace is gradually raised ~50 ^{0}C above the melting temperature of the compound over 3-4 hours. The temperature of the upper ‘‘cold’’ zone of the furnace was 650 K, which is slightly below the boiling point of sulfur (718 K [23]), and the lower ‘‘hot’’ zone was 30^0–50^0 higher than the melting point of the synthesized compound. After synthesis, the ampoule was kept at 750 K for 100 h. The phase purity of the synthesized compound was controlled by the differential thermal analysis (DTA) and the powder X-ray diffraction (PXRD) technique. Figure 1 shows the DTA heating curve and PXRD pattern of the synthesized RT-Cu_3SbS_3 compound. The melting point determined from the DTA heating curve practically coincided with the literature data. This diffraction pattern is identical with the one given in the database of the Bruker software. By indexing the diffraction pattern, we obtained lattice constants of crystallographic parameters of this compounds which substantially coincide with the published data [24,25].

a)



b)

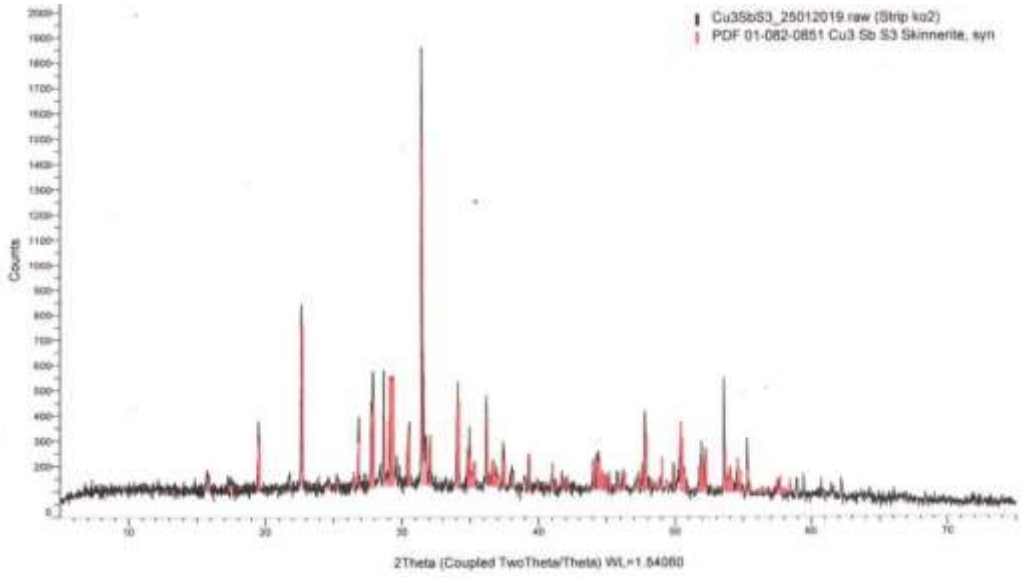


Fig. 1. The DTA heating curve (a) and the PXRD pattern (b) of the synthesized ternary compound Cu_3SbS_3

Samples of the Cu_3SbS_3-CuI system with different compositions were prepared by co-melting of appropriate amounts of the previously synthesized and identified ternary Cu_3SbS_3 compound with binary CuI in quartz ampoules. Synthesized samples were powdered and subjected to long-term thermal treatment at 30-50^0 below the solidus.

Obtained equilibrium samples were studied by the PXRD analysis using a D8 ADVANCE diffractometer with $CuK_{\alpha 1}$ radiation. TOPAS 4.2 and EVA computer programs were used to determine the crystal lattice parameters.

DTA was used for identification of the pre-synthesized Cu_3SbS_3 ternary compound in evacuated quartz ampoule on a differential scanning calorimeter 404 F1 Pegasus System (NETZSCH). The measurement results were processed using the NETZSCH Proteus Software. Accuracy of the temperature measurements was within ± 2 K.

Results and dıscussıon

The results of the powder X-ray diffraction analysis of the equilibrium samples of Cu_3SbS_3-CuI system are given in the figure 2. As can be clearly seen, the sample containing 66.7 mol% CuI has a diffraction pattern that is not characteristic of the original compounds, and in alloys rich in copper (I) iodide (≤ 66.7 mol% CuI), the diffraction lines of the CuI compound are also added to the picture.

A comparative analysis of the X-ray diffraction pattern of a sample containing 66.7 mol% CuI with literature data shows that it corresponds to a compound of the $Cu_5SbS_3I_2$ composition and crystallizes in an orthorhombic system with space group *Pnnm*. The lattice constants calculated by us for the sample containing 66.7 mol% CuI are almost identical to the literature data [26] of the four-component $Cu_5SbS_3I_2$ compound (*a = 10.4670 (20), b=12.8370 (20), c = 7.6540 (20) Å; Z=4*).

The X-ray diffraction patterns of the samples from the area rich in Cu_3SbS_3 (≥66.7 mol% CuI) of the Cu_3SbS_3-CuI system have more complex diffraction patterns (fig.2). This shows that the system in that area is unstable and characterized

by complex physico-chemical interaction of initial phases.

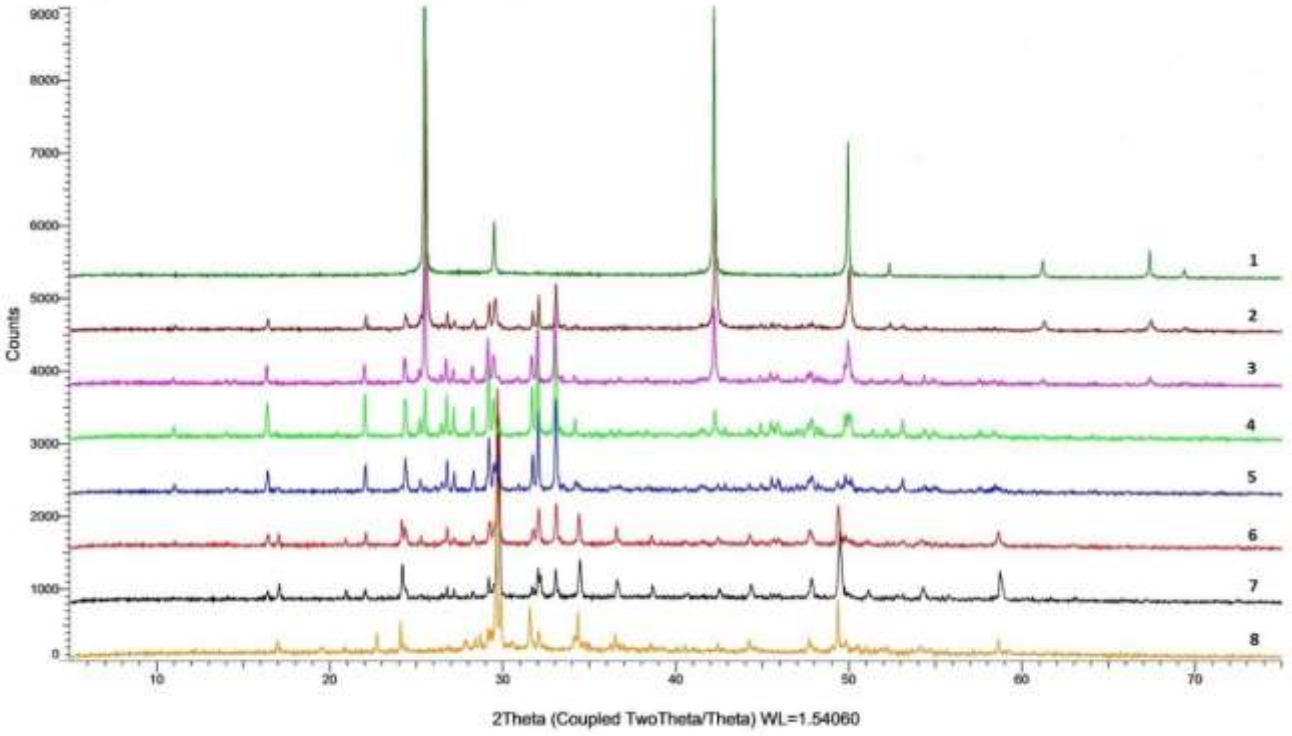


Fig. 2. The PXRD patterns of some alloys of the system Cu_3SbS_3-CuI : 1 – CuI, 2 – 90 mol% CuI, 3 – 80 mol% CuI; 4 – 66.7 mol% CuI, 5 – 60 mol% CuI; 6 – 40 mol% CuI; 7 – 20 mol% CuI, 8 – Cu_3SbS_3

Thus, based on the experimental observations in this work, we have studied the interaction of components in the Cu_3SbS_3-CuI system at room temperature by means of PXRD analysis. It was identified, that, the system is characterized by the formation of one quaternary compound $Cu_5SbS_3I_2$ and a complex interaction between initial binary and ternary compounds.

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Cu_3SbS_3-CuI SİSTEMİNİN RENTGENOQRAFİK TƏDQİQİ

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Xülasə: Cu_3SbS_3-CuI binar sistemində faza tarazlığının təbiəti tam qatılıq intervalında ilk dəfə olaraq rentgen faza analizi vasitəsilə öyrənilmişdir. Müəyyən edilmişdir ki, tərkibində 66,7 mol.% CuI olan nümunə bir fazadan ibarət olub tədqiq olunan sistemi təşkil edən ilkin fazalardan tamamilə fərqlənən yeni difraksiya mənzərəsinə malikdir. TOPAS 4.2 və EVA kompüter proqramlarından istifadə etməklə bu nümunənin rentgen difraksiya nümunəsi əsasında təyin edilmiş kristal qəfəs növü və parametrləri $Cu_5SbS_3I_2$ dördkomponentli birləşməsi üçün ədəbiyyat məlumatları ilə tam üst-üstə düşür. Sistemin mis (I) yodidlə zəngin nümunələri $Cu_5SbS_3I_2$ və CuI fazalarının ikifazalı qarışığından ibarətdir. Həmçinin, sistem $Cu_5SbS_3I_2$-Cu_3SbS_3 qatılıq intervalında qeyri-stabildir və ilkin komponentlərin mürəkkəb fiziki-kimyəvi qarşılıqlı təsiri ilə xarakterizə olunur.

Açar sözlər: Cu_3SbS_3-CuI sistemi, faza tarazlıqları, qəfəs parametrləti, rentgen-faza analizi

РЕНТГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ СИСТЕМЫ Cu_3SbS_3-CuI

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Аннотация: *Методом рентгенофазового анализа (РФА) впервые изучен характер фазовых равновесий в бинарной системе Cu_3SbS_3-CuI во всем диапазоне концентраций при комнатной температуре. Установлено, что образец, содержащий 66.7 мол. % CuI, состоит из одной фазы и имеет порошковую дифрактограмму, совершенно отличную от составляющих фаз исследуемой системы. Тип и параметры кристаллической решетки, определенные на основании рентгенограммы этого образца с помощью компьютерных программ TOPAS 4.2 и EVA, полностью соответствуют литературным данным четырехкомпонентного соединения $Cu_5SbS_3I_2$. Богатые иодидом меди (I) образцы системы состоят из двухфазной смеси фаз $Cu_5SbS_3I_2$ и CuI. Однако в интервале составов $Cu_5SbS_3I_2$–Cu_3SbS_3 система неустойчива. В этом интервале концентраций система характеризуется сложным физико-химическим взаимодействием исходных компонентов.*

Ключевые слова: *система Cu_3SbS_3-CuI, фазовые равновесия, параметры решетки, РФА.*